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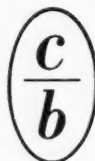
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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab. - Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. - Publisher.

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THE PRESENT STATE OF THE NITROGENOUS FERTILIZER INDUSTRY IN THE USSR AND ABROAD

V. A. Klevke

The importance of mineral fertilizers as the main means for raising the productivity of agricultural crops is very great.

By the directives of the XXth Assembly of the CPSU on the Sixth Five-Year Plan for the development of the national economy of the USSR, the volume of production of mineral fertilizers (calculated in nominal units) must be raised to 19,600,000 tons in 1960.

According to Academician D. N. Prianishnikov's calculations, the value of the annual increase in the production of cotton, sugar beet, flax, and tea obtained at a cost of 600,000,000 rubles for mineral fertilizers is 4,000,000,000 rubles.

The increases in agricultural yields by the use of mineral fertilizers are also illustrated by the following data [1]:

Crop increase (in kg per 1 kg of nutrients)

	N	P ₂ O ₅	K ₂ O
Winter wheat (grain)	12-15	7-8	3-4
Raw cotton	10-12	5-6	2
Flax (fiber)	2-2.5	2	1.5
Sugar beet (roots)	120-160	50-55	40-50
Potatoes	120	40-50	40-50

The most important nutrients introduced into the soil in the form of mineral fertilizers are nitrogen, phosphorus, and potassium; the mineral fertilizers produced by the chemical industry are accordingly classified as nitrogen, phosphorus, and potash fertilizers. Mixed fertilizers are also produced, containing two nutrient elements (such as nitrogen and potash, or nitrogen and phosphorus), or even all three.

Among the wide range of mineral fertilizers a leading position in effectiveness is held by nitrogenous fertilizers, but the supply of these falls considerably short of the agricultural demand.

The modern range of the most important nitrogenous fertilizers produced in the Soviet Union and abroad is given below and in Table 1 [2].

Contents of nutrient substances (%)

	N	P ₂ O ₅	K ₂ O
Ammoniacal			
Ammonium sulfate	20.5-21	—	—
Ammono-phos	11	47	—
Ammonia	82	—	—
Ammonia liquor	20-22	—	—

	N	P ₂ O ₅	K ₂ O
Nitrate			
Sodium nitrate	16	—	—
Calcium nitrate	13–15.5	—	—
Potassium nitrate	13.8	—	46.5
Ammonia nitrate			
Ammonium nitrate	34.5	—	—
Calcium ammonium nitrate	20.5	—	—
Nitrophosphate	14–20	14–22	—
Mixed N–P–K ("Nitrofoska")	11.5–15.7	11.5–15.7	11.5–15.7
Ammoniates			
Based on ammonium nitrate	34–41	—	—
Based on urea	37.0–45.5	—	—
Amides			
Calcium cyanamide	18.5–20	—	—
Urea	46	—	—

TABLE 1

Breakdown of Nitrogen Fertilizers Produced in the Capitalist Countries During 1952–1955

Where and when produced	Total fertilizer produced (in tons nitrogen × 10 ⁶)	In various forms (by % nitrogen content)							
		ammonium sulfate	ammonium nitrate (solid) *	calcium nitrate	sodium nitrate	calcium cyanamide	liquid **	other solids (urea, mixed fertilizers)	organic fertilizers (on the market)
All capitalist countries									
In 1952–1953 . .	4.58	34.1	23.6	6.1	5.1	7.0	13.8	8.8	1.5
In 1953–1954 . .	5.11	32.9	26.2	6.6	5.1	5.4	15.7	6.4	1.7
In 1954–1955 . .	5.60	32.5	27.3	6.4	4.7	5.1	15.1	7.5	1.4
Including 1954–1955 in countries of:									
Europe	2.69	31.8	41.2	12.4	0.2	5.6	—	8.8	—
America	2.17	19.5	19.1	—	11.8	1.5	38.9	5.6	3.6
Asia	0.69	75.8	0.7	—	—	14.7	—	8.8	—

* Includes the production of calcium ammonium nitrate and ammonium sulfate–nitrate.

** Includes liquid fertilizers for mixing with other forms of mineral fertilizers, and also for direct introduction into the soil as ammonia, ammonia liquor, and ammoniates.

One of the oldest forms of nitrogen fertilizers is ammonium sulfate, the production of which came into use long before the introduction of ammonia synthesis from hydrogen and nitrogen.

At first ammonium sulfate was made from ammonia obtained as a by-product of the dry distillation of coal in the coke-oven and gas industries. Subsequently, with the introduction of the industrial process for producing ammonia from nitrogen and hydrogen (1913), the production of ammonium sulfate from synthetic ammonia grew rapidly.

The production of ammonium sulfate has been especially extensive in the capitalist countries. Of the total production of nitrogen fertilizers in the capitalist countries in 1954–1955, 5,600,000 tons calculated as nitrogen, 32.5% was ammonium sulfate. The proportion of ammonium sulfate in the total production of nitrogen fertilizers is particularly high in Italy, Great Britain, Japan and India.

However, ammonium sulfate is not a sufficiently concentrated nitrogen fertilizer. Large amounts of sulfuric acid are required for its production, and its cost per unit nitrogen content is high; moreover, this fertilizer has high potential acidity, and in acid soils it becomes ineffective after prolonged use.

The production of ammonium sulfate in the Soviet Union is confined to the conversion of ammonia extracted from coke-oven gas.

Ammonium sulfate represents a substantial proportion of the total output of nitrogen fertilizers in the USSR (2,984,000 tons calculated as ammonium sulfate [3]).

Ammonium nitrate. Ammonium nitrate has been the main nitrogen fertilizer in the USSR right from the start of development of the nitrogen-fertilizer industry. The USSR was the first country to organize the production of ammonium nitrate for use as a fertilizer in the pure form.

Ammonium nitrate is a concentrated fertilizer (34.5% N) of universal action, as it contains nitrogen in ammonia and nitrate forms; it is the most widely used nitrogen fertilizer in the USSR. Prolonged experience in the use of ammonium nitrate in the agriculture of the Soviet Union showed that it can be used in many regions of the country. The disadvantages of ammonium nitrate (explosion risk and caking) retarded the development of its production in a number of capitalist countries (Western Germany and others), and it was only on the basis of the successful experience of the USSR that the production of ammonium nitrate as fertilizer was extensively developed during the post-war period, mainly in the U.S.A., and later in some other countries.

Until quite recently ammonium nitrate was not supplied in pure form for agricultural purposes in the capitalist countries, as before the Second World War the use of pure ammonium nitrate as fertilizer was illegal in most capitalist countries.

This prohibition was the consequence of the tremendous explosion which occurred in Oppau in 1921, caused by detonation of ammonium nitrate (4500 tons) which had caked in storage. Some small explosions were reported in other foreign countries.

Because of this, the nitrogen industries of the capitalist countries produced, during that time, either a mechanical mixture of ammonium nitrate with ammonium sulfate (26% nitrogen), or calcium ammonium nitrate (20.5% nitrogen), made by crystallization of a melt of ammonium nitrate with ground limestone.

After the Second World War great possibilities arose for the production of pure ammonium nitrate, and the demands of agriculture for nitrogen fertilizers increased; consequently the nitrogen industry of the U.S.A., and later of other countries, commenced mass production of pure ammonium nitrate, together with research in ways of improving the physical properties of this fertilizer.

Recently the production of ammonium nitrate, calculated as combined nitrogen, has outstripped the production of ammonium sulfate in a number of countries.

Data for U.S.A. and France are significant in this respect (Tables 2 and 3).

The wide adoption of ammonium nitrate in agricultural practice has been greatly aided by the favorable results of many years of research and trials, both in the USSR and abroad, on the reduction of certain adverse properties of ammonium nitrate (caking and hygroscopicity).

It has now been established that there are two main causes of the caking of ammonium nitrate.

1. When hot ammonium nitrate cools in bags, and during prolonged storage when the salt undergoes humidification followed by drying, ammonium nitrate crystallizes out of the mother liquor. The crystals which separate out of the solution on the particle surfaces bind adjacent particles together, i.e., cause caking [4, 5]. This effect is favored by the relatively high solubility of ammonium nitrate in water [6], the high temperature coefficient of solubility, and the hygroscopicity of the salt [7].

2. Ammonium nitrate exists in several modifications [8]. When the hot salt cools in bags, it undergoes a transition at 32.27°. The rearrangement of the crystal lattice in this transition under pressure is accompanied by caking [9].

One of the most effective measures for the prevention of caking is to decrease the active surface of the salt by treatment with a water-repellent substance [10]. However, this method was not widely adopted

because of the fire and explosion risk, and was strictly forbidden (U.S.A) after explosions of ammonium nitrate in Texas City and Brest [11].

Many of the proposed methods for decreasing caking involve the use of various mineral powdered additives for coating the salt particles [12, 13]. Some of these additives merely decrease the active surface of the particles; others also have adsorptive properties.

TABLE 2

U.S.A. Production of Ammonium Nitrate and Ammonium Sulfate for Use as Agricultural Fertilizers

Year	Ammonium nitrate, solid and in solution (tons of nitrogen $\times 1000$)	Ammonium sulfate	
		total (tons of nitrogen $\times 1000$)	from synthetic ammonia (tons of nitrogen $\times 1000$)
1951	339	280	115
1952	374	298	150
1953	398	284	107
1954	486	325	177
1955	507	390	211

TABLE 3

Production of Nitrogen Fertilizers in France

Type of fertilizer	Amount (in tons of nitrogen $\times 1000$) produced during			
	1938	1948	1952	1953/54
Fertilizers from synthetic ammonia				
Containing ammonia nitrogen	48	45	46	36
Containing nitrate nitrogen	41	32	38	34
Containing ammonia and nitrate nitrogen	52	68	131	140
Mixed	—	24	35	47
Other fertilizers (ammonium sulfate from by-product ammonia, calcium cyanamide)	36	24	35	35

However, such dusting additives gradually migrate from the surface into the particles, and the salt surface regains its original properties; i.e., processes of moisture adsorption and desorption are fully resumed [14].

Moreover, the action of additives with adsorptive properties is limited by their capacity for moisture. Thus, the effect produced by dusting additives should be regarded as temporary.

Whetstone [5] has proposed the addition of very small amounts of dyes, which influence the form of the crystals and confer brittleness on them, to salts which tend to cake. The amounts added are 0.01-0.03% by the weight of the salt, and the explosion risk of ammonium nitrate is not increased. However, dyes do not completely prevent the caking of ammonium nitrate, and their effectiveness diminishes appreciably with increasing amounts of absorbed moisture, i.e., with dilution.

The recent literature also contains papers and patents in which the use of surface-active additives is recommended [5, 15]. However, the use of such additives is restricted by their relatively high cost.

Another method for decreasing the caking of ammonium nitrate which is worthy of attention is cooling before bagging. Cooling of ammonium nitrate, especially the granulated salt, before bagging is a very effective measure which is directed against both the causes of caking. If the packages used are airtight, ammonium nitrate cooled to 30° and below remains free-running for a long time [16].

In foreign practice the last stage before packaging of the salt is always cooling, irrespective of the means used for reducing caking [17].

Caking of the salt is appreciably reduced by a change of the particle shape from finely crystalline to granulated [12].

In recent years calcium and magnesium nitrates and tricalcium phosphate, i.e., the products obtained by nitric acid decomposition of phosphates and dolomites, have been widely used in Russian practice for the prevention of caking of ammonium nitrate. The additives comprise 0.3-0.5% P_2O_5 , 0.1-0.2% calcium and magnesium nitrates (calculated as CaO).

Various explanations are given in the literature for the effect of inorganic additives in preventing the caking of ammonium nitrate; however, some facts are certain, namely: in presence of these additives the solubility of ammonium nitrate decreases, and therefore less salt crystals are deposited from a saturated solution on cooling or drying. The additives assist migration of moisture from the surface into the particles, and this also tends to decrease caking.

Additives influence the transition temperatures of the different forms of ammonium nitrate, and decrease the vapor pressure of saturated NH_4NO_3 solution, etc. All these changes decrease the caking of ammonium nitrate.

The principal stages in the industrial process for the production of ammonium nitrate are neutralization, evaporation, crystallization or granulation, drying, and packing.

The separate stages of ammonium nitrate production in Russian plants are now at an advanced technological level.

Large-scale equipment and continuous processes are to be adopted in the planned ammonium-nitrate plants in the Soviet Union. ITN units with an output of 250-350 tons/day are to be replaced by units producing 700 tons/day. Vertical evaporators with 500 m² surface area are to be used, which doubles the heating surface available with horizontal evaporators. By the installation of larger equipment, the number of units, ducts and fixtures can be reduced considerably, as can the maintenance staff, production areas and volumes of the buildings.

Comparative floor areas and volumes of buildings required for a unit with a nominal output of 450,000 tons of ammonium nitrate per annum are given below.

	Without larger equipment	With larger equipment	Reduction (%)
Total area (m ²)	15425	12422	19.5
Total volume (m ³)	114636	88726	22.5

Automation is extensively used in the production of ammonium nitrate, making operation better and cheaper.

To cheapen the construction of graining towers, pumps are being designed in our national industry for conveying ammonium nitrate melts. Preliminary trials of some types of pumps suggest that it may be possible to design graining towers without superstructures. This would make the towers lighter and cheaper.

A more efficient melt-spraying device is being developed for more complete utilization of the effective area of the graining tower. The problems of complete cooling of the ammonium nitrate in the graining tower, and similar problems, are being solved.

* Transliteration of Russian — Publisher's note.

The necessity for the wide adoption of new and efficient processes and high-productivity equipment, and for reduction of costs in the nitrogen industry raises other problems relating to the production of ammonium nitrate. These include the production of ammonium nitrate without the use of evaporators; this would give a finished 98-99% melt from the ITN apparatus which could be gained directly.

The Stengel process, operated on the industrial scale since 1953 in the U.S.A., which does not use evaporators, is of interest in this connection.

According to published data [18], hot nitric acid and ammonia in the stoichiometric proportions are fed into a tubular neutralizer 0.4 m in diameter and 3 m high, operating under slight excess pressure. The neutralization proceeds very rapidly in a weakly alkaline medium. The temperature of the solution in the reactor, which reaches 205-234°, is regulated by preheating the reactants.

The vapor-liquid mixture formed in the neutralizer is separated into vapor and melt; the concentration of the latter reaches 98%. Hot air (205°) is then blown through the melt in a special apparatus, reducing the moisture content of the melt to 0.02%.

The almost completely dehydrated melt is fed onto continuously moving metal bands, cooled by water on the inside, on which the salt crystallizes in the form of scales.

According to later literature data [19], improvements have been introduced in the Stengel process; the ammonium nitrate melt passes from the neutralizer directly to the graining tower, which simplifies the earlier process considerably. The advantages of this process include a reduction of the capital investment in the building of ammonium nitrate plants, as the construction of evaporator sections becomes unnecessary. However, this process may involve somewhat higher losses of ammonium nitrate and nitric acid, because at the high reaction temperatures, above 200°, ammonium nitrate is formed in the form of a mist which is difficult to trap, and partial decomposition of nitric acid and ammonium nitrate takes place.

Nitrates. Only a small proportion of the nitrogen fertilizers made in our country consists of pure nitrates (sodium, potassium, and calcium nitrates).

Sodium and calcium nitrates are mainly made by absorption of nitrogen oxides, after acid absorption, in sodium carbonate solution or milk of lime respectively; potassium nitrate is made by a conversion process from potassium chloride and sodium nitrate. Sodium nitrate now represents about 5% of the total production of nitrogen fertilizers in the capitalist countries. The production of calcium nitrate is somewhat greater (in terms of nitrogen); it is about 7% of the total production of nitrogen fertilizers.

Half the world output of calcium nitrate is produced in Norway, and relatively large amounts are made in Italy, Western Germany, France, and Holland. Calcium nitrate production was also organized in the first nitrogen works in Egypt, brought into operation after the Second World War.

A certain amount of calcium nitrate is obtained as a by-product in the production of nitrophosphates by the decomposition of phosphates by nitric acid. The agricultural demand for sodium nitrate is almost satisfied by the natural product, while the synthetic salt, made in very much smaller amounts, is used for industrial purposes when a more pure product is required.

In most foreign countries sodium nitrate is made by treatment of soda ash with nitric acid, either by absorption of nitric acid in soda solution, or by absorption of nitrogen oxides in soda solution.

In one Norwegian plant (Eidanger) sodium nitrate is made from calcium nitrate by cation exchange. Sea water is the source of Na ions in this process.

Calcium cyanamide is not inferior to ammonium sulfate as a fertilizer in a number of cases. Calcium cyanamide is as effective as ammonium sulfate on neutral soils. On acid podzols calcium cyanamide is a more effective fertilizer than ammonium sulfate, as it contains lime which reduces the soil acidity.

The present outputs of calcium cyanamide and calcium nitrate for agricultural purposes in foreign countries are almost equal (in terms of nitrogen). However, in some foreign countries there is a tendency to reduce the scale of production of calcium cyanamide somewhat, owing to the higher cost of the nitrogen in it relative to other types of nitrogen fertilizers made from synthetic ammonia.

Calcium cyanamide is produced in considerable amounts in Canada, Western Germany, Japan and Italy.

Urea. In addition to the increased output of ammonium nitrate, the production of synthetic urea from ammonia and carbon dioxide has increased during the postwar period in the fertilizer industries of the capitalist countries. Urea is one of the most highly concentrated nitrogen fertilizers, containing 46% nitrogen (100 kg of urea is equivalent to 300 kg of sodium nitrate or 225 kg of ammonium sulfate). In our country urea is used on a small scale as an independent fertilizer, owing to its high cost.

The present world production of urea is about 600,000-700,000 tons per year; published information on the construction and starting of new large plants for urea production indicates that it is intended to increase the output in the near future.

Before the Second World War urea for fertilizers was made in only one plant, which produced urea solution for use in the production of mixed fertilizers, whereas in 1954 the production of urea in the capitalist countries exceeded 1000 tons per day.

In 1955 the production of urea reached 1500 tons/day.

The growth of urea production in a number of capitalist countries is illustrated by the data below.

Production of urea 1946-1955 (in thousands of tons)

	1946	1948	1950	1951	1952	1953	1954
England	9.6	11.8	35.2	41.2	41.3	—	—
Italy	—	4.0	6.0	8.9	10.9	22.2	24.4
Japan	0.5	1.4	16.5	33.0	56.4	77.9	121.0
Norway	—	—	—	—	8.3	8.9	112.5
Holland	—	—	—	—	2.2	17.2	15.0
India	—	—	—	—	—	—	0.5

In 1955 in the U.S.A. there were five plants producing urea, with a total annual capacity of 450,000 tons. In 1956 about 300,000 tons of urea was produced; 60% of this was for fertilizers, 21% for addition to cattle fodder, and 19% for plastics production.

By the end of 1956, with two more plants brought into operation, the total U.S.A. capacity for urea production should be over 500,000 tons per annum. Urea is made in large amounts in Japan, Great Britain, Italy, the Federal German Republic, Norway, the Netherlands, France, and other countries.

In Japan, the total capacity of the urea-synthesis plants was 150,000 tons even in 1953, and it is intended to raise this to 300,000 tons per annum within the next few years. 59,000 tons of urea was produced in Italy in 1955. According to preliminary data, the present production of urea is 100,000 tons per annum in Western Germany and 50,000 tons in Great Britain.

The production of urea consists of the following stages: synthesis of urea from CO_2 and NH_3 , distillation of the synthesis products (urea melt), with subsequent conversion of the urea solutions into the dry product and recovery of the distillation gases (ammonia and CO_2). The technological processes for urea production differ mainly in the methods used for utilization of the distillation gases.

In the one-stage distillation process all the ammonia present in the gases distilled from the melt is absorbed in nitric or sulfuric acid to give ammonium nitrate or ammonium sulfate.

In this relatively simple process the direct utilization of the starting materials (for urea synthesis) is low, and it requires a large expenditure of heat for evaporation of the ammonium nitrate solution formed. In one-stage distillation 5-7.5 tons of NH_4NO_3 is obtained in the form of 60% solution per ton of urea produced, so that the production of urea must be combined with the production of much larger amounts of ammonium nitrate. For large plants producing a narrow range of fertilizers it is more economic to use processes with recycling of the distillation gases in some way into the urea-synthesis cycle. Examples of such processes include the following:

1) Hot compression. The gaseous mixture of unreacted ammonia and carbon dioxide is compressed at 175-210° and fed into the synthesis tower together with fresh ammonia and carbon dioxide. According to some specialists the method is uneconomic, although it gives 93% conversion of ammonia. The defects of the method include high capital cost, difficult operation, and considerable corrosion of the plant. The process is operated on a large scale in Ludwigshafen.

2) Recycling of unreacted ammonia and carbon dioxide in the form of aqueous solution. In this case the adverse effect of water is compensated by an increase of the ammonia-carbon dioxide ratio and by the use of higher temperatures and pressures. After the reaction in the synthesis tower, the mixture (urea, water, ammonia, and ammonium carbamate) is distilled twice, with liberation of excess ammonia (Stage I) and decomposition of residual ammonium carbamate (Stage II). The process is operated by the American Du Pont company at Belle.

3) Recycling of ammonia and carbon dioxide in the form of a suspension of ammonium carbamate in mineral oil (Pechiney process). According to the French company "ATS", this process provides a good solution to the problem of recycling of unreacted ammonia and carbon dioxide, avoids corrosion of the equipment, and makes it possible to regulate the temperature in the reactor by means of the mineral oil. The process is operated in two plants in U.S.A., in Pryor (Oklahoma), and in Memphis (Tennessee).

Several processes involve the selective absorption of ammonia or carbon dioxide. These include the Inventa process (of the Swiss Hovag company). In this process the gas mixture (NH_3 and CO_2) is washed with aqueous urea nitrate solution; the ammonia is absorbed and the carbon dioxide is released into the atmosphere or recycled. According to some Japanese patents aqueous 23% monoammonium phosphate solution is used for similar selective absorption. The diammonium phosphate solution formed by absorption of ammonia is regenerated with recovery of 95.7% of ammonia, leaving monoammonium phosphate solution which is recycled.

In the Chemico process, monoethanolamine and some other substances are used for selective absorption of carbon dioxide.

The production of urea in the USSR is not sufficiently developed. The factory production is used mainly for industrial purposes.

In connection with the proposed large-scale expansion of urea production in the USSR work is in progress on technical and economic evaluation of different processes for the production of urea and on selection of the most rational process.

Liquid nitrogenous fertilizers. Liquid fertilizers, in the form of aqueous solutions of various fertilizer salts, solutions of salts in ammonia (ammoniates), liquid ammonia, and ammonia liquor are becoming increasingly used in recent years in the agriculture of a number of foreign countries, and on an experimental scale in the USSR. Most of the liquid fertilizers used are based on ammonia.

The total U.S.A. production of liquid fertilizers, both for mixed fertilizers and for direct use, exceeded 800,000 tons of nitrogen in 1954-1955; this was over 50% of the total U.S.A. production of nitrogen fertilizers during this period. The ammoniates used in the U.S.A. include solutions based on ammonium nitrate, with total nitrogen contents from 37.0 to 49%, and based on urea with total nitrogen contents up to 45.5%.

Recently ammoniates based on ammonium nitrate and urea, with up to 53% total nitrogen, have also been used. Ammonia and ammonia liquor are extensively used.

The reason is that plants effectively assimilate part of the anhydrous ammonia directly, while part is assimilated by the action of nitrifying bacteria, in the form of nitrates.

However, it has been pointed out [20, 21] that the prolonged use of ammonia as a fertilizer has certain disadvantages. It is noted that, since ammonia is the most concentrated form of fertilizer, it raises soil acidity after oxidation by microorganisms.

It is recommended to use anhydrous ammonia as a source of nitrogen in complete liquid fertilizers.

The economic advantage of the use of liquid fertilizers became especially evident after it had been confirmed in practice that the agricultural effect produced by liquid fertilizers (ammonia) is not inferior to that produced by solid fertilizers. To this, other advantages of liquid fertilizers should be added; savings in

paper containers; elimination of such adverse properties of solid fertilizers as hygroscopicity, caking, and segregation; and more regular and exact distribution of the fertilizer in the soil.

The cost of unit nitrogen is 25-35% lower in liquid nitrogenous fertilizers than in solid fertilizers such as ammonium nitrate. The selling price of nitrogen in anhydrous ammonia is $\frac{2}{3}$ to $\frac{1}{2}$ of the price in solid fertilizers in the U.S.A.; in ammonia liquor it is lower still.

The production of liquid nitrogenous fertilizers (ammonia, and ammonia liquor) makes it possible to accelerate the construction of "short-process" nitrogen plants, without units for the conversion of ammonia into nitric acid and ammonium nitrate.

This reduces the construction work necessary for power supplies, transport, storage, auxiliary services, and living accommodation.

As a result the capital saving in the construction of a nitrogen plant with an annual capacity of 100,000 tons of ammonia may be up to 170,000,000-180,000,000 rubles for the plant itself, and 7,000 tons of metal (including 2,000 tons of the scarce stainless steel).

The extensive use of liquid fertilizers involves certain difficulties. The use of liquid fertilizers necessitates: 1) construction of special stores, hundreds of thousands of cubic meters in capacity, in the industry and agriculture; 2) increased transportation capacity; 3) the production of special machines and cultivators for introducing liquid fertilizers into the soil.

However, if these problems are successfully solved, liquid fertilizers are preferable.

In summer 1956, trials of the use of liquid nitrogenous fertilizers were carried out in the Ukraine and the Uzbek SSR. The following quantities were applied during spring and summer to an area of 12,000 hectares, and in the fall to an area of 2,000 hectares, including 8,000 hectares in collective farms and 6,000 hectares in state farms:

Liquid ammonia and ammoniates containing (%)

	A	B	C
NH_4NO_3	64-67	53-56	27-30
NH_3	14-17	23-26	18-20
H_2O	22-16	24-18	30-22
$\text{Ca}(\text{NO}_3)_2$	—	—	25-28
N content	34-37.5	37.5-41	30.5-31.6

for cotton in the Uzbek SSR, and for sugar beet, maize, vegetables, and other crops mainly as a supplementary feed in the Ukrainian SSR.

The preliminary results of the trials of the use of liquid fertilizers are quite encouraging; it is therefore proposed in 1957 to carry out trials with liquid nitrogenous fertilizers in collective and state farms of the RSFSR, the Ukrainian SSR, and the Kazakh SSR, over an area of not less than 65,000 hectares.

In future work on the use of liquid fertilizers the main attention must be devoted to the development of designs for home-produced machines for the application of liquid fertilizers, the formulation of the most economic scheme for the supply of liquid nitrogenous fertilizers to agriculture, and more accurate determination of the economic effectiveness of their use.

Another fundamental task is the development of new compositions of liquid fertilizers, containing phosphorus and potash in addition to nitrogen.

At present, if liquid nitrogenous fertilizers are used, nitrogen, phosphorus, and potash must be introduced separately (in at least two stages); this involves additional labor for application of the fertilizers before sowing and during supplementary feeding.

Special attention must be devoted to a search for inhibitors for reducing corrosion, by decreasing the vapor pressure of ammonia over the solutions at elevated temperatures. In view of the fact that storing liquid

ammonia involves a number of difficulties (pressure stores are needed), it may be more advantageous at first to use ammonia liquor (20-25%) as liquid nitrogenous fertilizer. The production of ammonia liquor should be organized in the consuming regions, with liquid ammonia delivered there.

The production of ammoniates is not as economic as that of ammonia liquor; therefore it can be regarded as unpromising at present, and should be restricted to a small scale for special needs.

The nitrogen industry of the Soviet Union, which is developing in accordance with the national economic plan, is characterized by a high rate of growth, necessary for the speediest satisfaction of the growing needs of the national economy.

For extension of the range of nitrogen fertilizers in the USSR it is intended to develop the production of physiologically alkaline forms of fertilizers (including calcium nitrate), to increase the production of mixed fertilizers and of urea, and to organize the production of liquid nitrogenous fertilizers in the form of ammonia and ammonia liquor.

The nitrogen industry has at its disposal many research workers, engineers, technologists, and inventors, capable of carrying out honorably the tasks set by the XXth Assembly of the CPSU.

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A STUDY OF THE ROASTING OF CARBONACEOUS PYRITES

S. A. Amirova, V. V. Pechkovskii, and V. V. Parkacheva

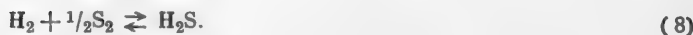
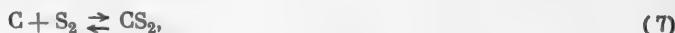
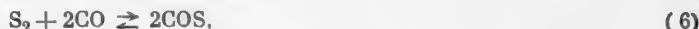
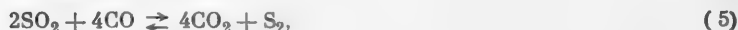
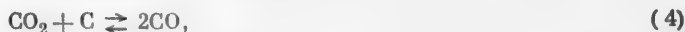
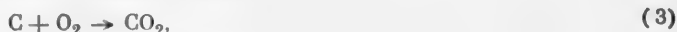
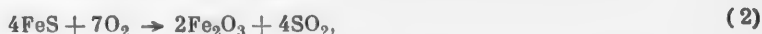
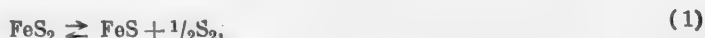
(The A. M. Gor'kii State University, Perm')

Processes involving the roasting of iron disulfide containing varying amounts of carbon are used in the production of sulfuric acid and sulfur, in the smelting of copper and nickel ores, and in the sintering of pyrites [1-6].

Studies of the roasting of iron disulfide with carbon are also of interest in relation to some aspects of the behavior of sulfur compounds in the coking process [7].

Mixtures of iron disulfide and coal, obtained as a waste product in the mining and beneficiation of coals, are generally called carbonaceous pyrites. Unbeneficiated carbonaceous pyrites contains 34-40% of sulfur and 12-15% of coal, and the concentrated product contains 47-48% of sulfur and 5-6% of coal [1]. Numerous processes may occur during the roasting of carbonaceous pyrites, including coking of the coal, combustion of the carbon, dissociation of the pyrites, oxidation of iron sulfide, reduction of sulfur dioxide, and reactions of elemental sulfur with hydrogen, carbon, and carbon monoxide.

Some of the most important reactions taking place during the roasting of carbonaceous pyrites in a stream of air can be schematically represented by the following equations:



The final result of the roasting of carbonaceous pyrites (the proportions of sulfur and carbon burned out, the composition of the gases formed) depends on numerous factors which influence the rate and extent of the reactions comprising the process.

The present investigation was undertaken in order to determine the influence of certain factors on the roasting of carbonaceous pyrites.

The object was to study how the degree of combustion of sulfur and carbon in carbonaceous pyrites depends on the temperature, the carbon content and the presence of impurities in the original mixture, time, and the oxygen concentration of the original gas.

EXPERIMENTAL METHODS

The material chosen for the study was carbonaceous pyrites from the Gubakha beneficiation plant, containing 37.79% of sulfur and 14.10% of carbon. The particle size of the pyrites used for the experiments was 0.25-0.50 mm.

1.0 g weighed samples of the pyrites were roasted at definite temperatures in a laboratory tube furnace in a stream of dry gas fed at 1 liter/hour. Air, pure oxygen, and air-oxygen mixtures were used.

For studies of the effects of carbon and admixtures on the roasting of carbonaceous pyrites coal and iron oxide were added to the pyrites.

The gases after the roasting were analyzed for different sulfur compounds, and the cinders for carbon and sulfur.

The principal experimental results are given in Tables 1-8 and Figs. 1-2. Data on the influence of temperature on the oxidation rate of carbonaceous pyrites in a current of air are presented in Table 1 and Fig. 1.

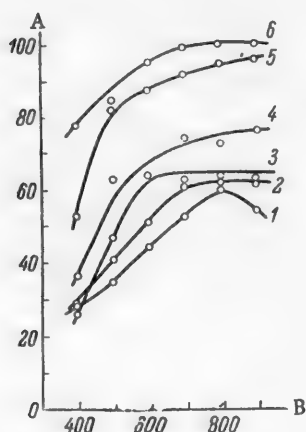


Fig. 1. Variation of the degree of oxidation of carbonaceous pyrites with temperature and oxygen content of the original gas ($\tau = 30$ minutes). A) Sulfur burned out of carbonaceous pyrites (%), B) temperature ($^{\circ}\text{C}$). Oxygen content of the original gas (in vol. %): 1) 21.0, 2) 31.4, 3) 37.5, 4) 49.4, 5) 77.7, 6) 100.0.

Therefore additions of pyrite cinders, which partially prevent sintering during the roasting of run-of-mine and flotation pyrites [1], must be regarded as undesirable in the roasting of carbonaceous pyrites.

The data in Tables 1 and 3 show that in general the rate of combustion of sulfur in carbonaceous pyrites decreases with increasing carbon content in the original mixture. For example, at 400° in 30 minutes, 29.1 and 12.4% of sulfur is burned out of pyrites containing 14.1 and 25.0% of carbon respectively. It is true that in the oxidation of pyrites containing 25.0% carbon at temperatures above 800° the roasting rate was somewhat higher than in the oxidation of pyrites with a lower carbon content. However, this merely indicates that the increase of the roasting rate under these conditions is caused by heating of the mixture owing to rapid oxidation of fairly large amounts of carbon.

The data in Tables 4 and 5 and Figs. 1 and 2 lead to the conclusion that the most important factor in raising the rate of oxidation of carbonaceous pyrites is an increase of the oxygen content of the original gas. For example, at 700° 52.7% of sulfur was burned out of carbonaceous pyrites in 30 minutes in a current of air, whereas 73.9 and 99.2% respectively was burned out during roasting in gases containing 49.4 and 100% oxygen.

The low rate of roasting of carbonaceous pyrites in a current of air must be specially emphasized. For example, at 800° only 59.8% of the sulfur was burned out of the pyrites in 30 minutes.

The data in Table 1 and Fig. 1 also show that the oxidation rate of carbonaceous pyrites increases with temperature up to 800° , and then decreases. This is caused by sintering of the carbonaceous pyrites in the $800-850^{\circ}$ range.

To study the possibility of prevention of sintering, experiments were carried out on the roasting of carbonaceous pyrites containing different amounts of iron oxide. However, as follows from the data in Table 2, additions of iron oxide decrease the roasting rate considerably without preventing sintering. Under equal conditions, the more iron oxide is added to the mixture, the less is the amount of sulfur burned out of the pyrites. This can probably be attributed to conversion of the ferric oxide to sulfide by the action of sulfur dioxide, according to the equation:



TABLE 1

Oxidation of Carbonaceous Pyrites in a Current of Air

τ	Sulfur burned out of carbonaceous pyrites (%) at temperature (°C)					
	400	500	600	700	800	900
5	16.1	19.5	24.1	44.5	52.4	48.0
10	18.9	22.4	35.0	49.6	53.5	51.7
15	—	29.3	37.9	49.8	54.7	54.6
30	29.1	34.5	44.0	52.7	59.8	55.8
50	44.7	47.7	56.7	64.1	68.7	65.8

TABLE 2

Oxidation of Carbonaceous Pyrites in a Current of Air, with Different Fe_2O_3 Contents in the Original Mixture ($\tau = 50$ minutes)

Amount of Fe_2O_3 added (%)	Sulfur burned out of carbonaceous pyrites (%) at temperature (°C)					
	400	500	600	700	800	900
5.0	39.9	47.0	59.8	61.0	58.7	51.5
10.0	14.1	16.9	34.0	49.5	46.8	40.8
20.0	9.9	15.1	26.6	35.9	34.9	31.6

TABLE 3

Oxidation of Carbonaceous pyrites in a Current of Air, with Different Carbon Contents in the Original Mixture ($\tau = 30$ minutes)

Carbon content of pyrites (%)	Sulfur burned out of carbonaceous pyrites (%) at temperature (°C)					
	400	500	600	700	800	900
20.0	27.7	31.0	37.4	47.7	50.6	51.0
25.0	12.4	18.1	23.6	47.8	65.0	57.8

It should be noted that if oxygen-enriched air is used in the roasting of carbonaceous pyrites sintering in the 800-900° range is avoided. It follows from the data in Table 4 and Fig. 1 that 31.4% of oxygen in the original gas is enough to prevent sintering of the carbonaceous pyrites.

Data on the composition of the gases formed during the roasting of carbonaceous pyrites are presented in Table 6.

It is seen that when carbonaceous pyrites is roasted in a current of air, the sulfur in the gaseous products is present as sulfur dioxide, hydrogen sulfide, carbon oxysulfide, and elemental sulfur. The relative proportions of the various gases in the mixture vary with the temperature. For example, at 400-500° sulfur dioxide and hydrogen sulfide predominate in the roasting gas, while above 800° the prevailing gases are hydrogen sulfide, carbon disulfide, and elemental sulfur.

The use of oxygen-enriched air alters the composition of the roasting gas fairly considerably. It follows from the data in Table 6 that the oxidation of carbonaceous pyrites with pure oxygen yields a gas in which, up to 700°, the sulfur is present mainly in the form of sulfur dioxide. Thus, when carbonaceous pyrites is roasted in pure oxygen and in air respectively at 700° for 30 minutes, 90.87 and 27.05% of the total oxidized sulfur is present in the roasting gases in the form of sulfur dioxide.

Data on the influence of duration of the experiment on the amount of sulfur burned out during the roasting of carbonaceous pyrites in a current of air are presented in Tables 1 and 5, and in Fig. 2. It is seen that the curves showing the relationship between the amount of sulfur burned out and the duration of the experiment differ somewhat for the roasting of pyrites in air and oxygen respectively. The form of Curve 2, Fig. 2, which represents the course of oxidation of carbonaceous pyrites in a current of oxygen, indicates that the rate of the process decreases steadily with time. In the oxidation of carbonaceous pyrites in a current of air, the sulfur combustion-time curve shows at least three characteristic periods (Curve 1, Fig. 2).

The first period, lasting about 5 minutes (under laboratory conditions), is characterized by rapid removal of sulfur from the pyrites. In the second period, lasting up to 30 minutes, the rate of the process is negligible.

Finally, in the third period, after about 30 minutes of roasting the amount of sulfur removed from the pyrites begins to increase again with time.

TABLE 4

Oxidation of Carbonaceous Pyrites in Gases of Different Oxygen Contents ($\tau = 30$ minutes)

Oxygen content of original gas (vol. %)	Sulfur burned out of carbonaceous pyrites (%) at temperature (°C)					
	400	500	600	700	800	900
31.4	29.0	41.0	51.3	61.4	62.3	62.0
37.4	26.1	47.3	64.6	62.3	63.2	62.8
49.4	36.2	62.6	65.1	73.9	72.2	76.7
77.7	53.0	81.8	87.2	91.7	94.5	95.5
100.0	77.4	84.2	95.0	99.2	100.0	100.0

TABLE 5

Oxidation of Carbonaceous Pyrites in a Current of Pure Oxygen

τ	Sulfur burned out of carbonaceous pyrites (%) at temperature (°C)					
	400	500	600	700	800	900
5	18.1	24.2	33.4	43.5	47.2	54.2
10	31.0	47.1	51.0	61.0	66.0	71.0
15	45.0	61.0	55.7	72.0	79.1	84.0
50	76.8	98.5	99.2	100.0	100.0	100.0

TABLE 6

Distribution of Sulfur Compounds in the Roasting Gases Formed at Different Temperatures ($\tau = 30$ minutes) Oxidation of carbonaceous pyrites in: 1) Air; 2) oxygen

Temperature (°C)	Pyrite sulfur converted into the gas phase in the form of (%)									
	SO ₂		H ₂ S		COS		CS ₂		S	
	1	2	1	2	1	2	1	2	1	2
400	86.08	84.38	13.10	1.12	0.20	0.65	0.64	0.30	0.00	13.55
500	85.81	91.29	9.00	0.48	0.23	0.52	0.33	0.07	4.54	7.64
600	50.71	99.90	5.05	0.00	0.23	0.03	0.91	0.07	43.10	0.00
700	27.05	90.87	8.47	0.00	0.42	0.39	3.64	0.54	60.42	8.20
800	12.00	75.83	20.75	0.00	0.76	0.57	8.15	1.20	58.34	22.40
900	8.56	55.56	31.30	1.90	1.11	1.59	12.15	3.55	51.88	37.40

These results can be explained by a consideration of the data on the rate of combustion of carbon in carbonaceous pyrites. It follows from the data in Table 7 and Fig. 3 that when carbonaceous pyrites is roasted in air, carbon is burned out relatively slowly. For example, about 1% of carbon remains in the pyrite even after 50 minutes at 900°. It also follows from the data of Table 7 and Fig. 3 that most of the carbon is burned out of the carbonaceous pyrites during the first 30 minutes, after which the rate of combustion of the carbon decreases.

This accounts for the data on the effect of time on the combustion rate of sulfur in carbonaceous pyrites given in Table 1 and Fig. 2. The first period in the roasting of carbonaceous pyrites in a current of air corresponds to removal of elemental sulfur from pyrites according to Equation (1), the second period, to combustion of carbon, and the third, to oxidation of iron sulfide after most of the carbon has been burned out. This shows once again that the presence of carbon in pyrites retards the oxidation of the latter considerably.

The data in Table 8 and Fig. 3 show that the rate of combustion of carbon in carbonaceous pyrites increases considerably with increasing oxygen content in the original gas. Thus, when carbonaceous pyrites is roasted for 30 minutes at 600° in air and oxygen respectively, 50.0 and 93.0% of carbon is burned out.

Thus, the rate of combustion of carbon, and consequently the rate of combustion of sulfur in carbonaceous pyrites is increased by the use of oxygen-enriched air.

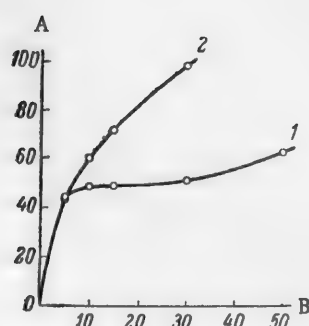


Fig. 2. Effect of time on the degree of oxidation of carbonaceous pyrites ($t = 700^\circ$). A) Sulfur burned out of the pyrites (%); B) time (minutes). Oxidation in a current of 1) air; 2) oxygen.

TABLE 7

Oxidation of Carbonaceous Pyrites in a Current of Air

τ	Carbon burned out of carbonaceous pyrites (%) at temperature ($^\circ\text{C}$)					
	400	500	600	700	800	900
5	5.3	14.3	18.3	18.5	34.9	38.2
10	12.1	29.3	37.0	53.8	55.5	65.5
30	30.0	45.8	50.0	66.5	74.5	79.5
50	39.4	53.2	58.5	68.8	85.3	95.0

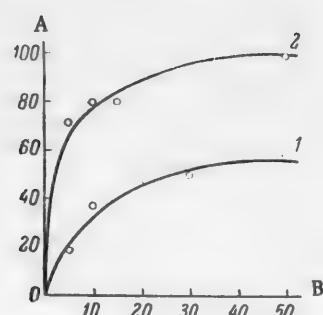


Fig. 3. Effect of time on the degree of oxidation of carbonaceous pyrites ($t = 600^\circ$). A) Carbon burned out of the pyrites (%); B) time (minutes). Oxidation in a current of 1) air; 2) oxygen.

TABLE 8

Oxidation of Carbonaceous Pyrites in a Current of Oxygen. Effect of temperature and time on the degree of combustion of carbon ($t = 600^\circ\text{C}$)

τ	5	10	15	30
Carbon burned out (%)	71.4	79.7	80.0	93.0

SUMMARY

1. It is shown that when carbonaceous pyrites is roasted in a current of air, combustion of sulfur and carbon occurs at a relatively low rate. It is noted that at about 800° sintering of the pyrites occurs, retarding the roasting.

2. Increase of the carbon content of the original mixture decreases the rate of sulfur combustion in the carbonaceous pyrites.

3. Additions of iron oxide to carbonaceous pyrites do not prevent sintering, and decrease the rate of sulfur combustion.

4. The rates of combustion of sulfur and carbon in carbonaceous pyrites are increased considerably if oxygen-enriched air is used. 31.4% of oxygen in the roasting gas is sufficient to prevent sintering in the 800 - 900° range.

5. When carbonaceous pyrites is roasted in a current of air, the sulfur is present in the roasting gas in the form of sulfur dioxide, hydrogen sulfide, carbon disulfide, carbon oxysulfide, and elemental sulfur. If oxygen-enriched air is used it is possible, under specific conditions, to obtain a gas in which the sulfur is present mainly in the form of sulfur dioxide.

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INFLUENCE OF INERT GASES ON THE SYNTHESIS OF AMMONIA*

V. I. Atroshchenko and N. A. Gavria

(The V. I. Lenin Polytechnic Institute, Khar'kov)

The production of pure nitrogen-hydrogen mixture, from natural gas and other sources, involves considerable difficulties. On the other hand, if nitrogen-hydrogen mixture with high content of methane and argon is used for the synthesis, the efficiency of the catalyst is low and therefore the actual process of ammonia synthesis becomes more complicated. It is therefore very important to determine conditions in which the cost of ammonia is reduced.

The influence of inert gases on ammonia synthesis has been studied by a number of workers. Toniolo and Giamarco [1], on the basis of Tour's work [2], constructed a nomogram for determination of the equilibrium ammonia contents. Vvedenskii [3] studied the influence of methane and argon in the synthesis of ammonia by a circulation process, using a high-activity catalyst. He noted that methane and argon both had the same effect on the ammonia yield, and recommended the use of the equilibrium equation for calculation of the ammonia content in the converted gas. Fazel [4] proposed an equation for calculation of the equilibrium ammonia content. Pastonesi [5] considered a cyclic synthesis process and attempted to derive an equation representing the influence of diluting inert gases as a function of their contents in the mixture.

A review of the papers cited shows that reliable experimental data for determination of the ammonia yield, and therefore of the catalyst productivity as a function of the methane and argon contents of the gas mixture entering the synthesis column, are not available. However, such data are necessary for calculations of material and economic balances for ammonia-synthesis processes using gas mixtures with high contents of inert gases.

The papers by Temkin and Pyzhev [6, 7], and by Temkin [8], are very significant in the field of the kinetics of ammonia synthesis. Temkin and Pyzhev [6, 7], Temkin and Kiperman [9], Eterman [10], Sidorov and Livshits [11, 12], and Sidorov, Markina, and Denisova [13] verified their equation experimentally. Rusov and Roiter [14], Roiter [15], and Vvedenskii [3] also studied the kinetics of ammonia synthesis. These investigations yielded valuable data, of theoretical and practical significance. However, these data were obtained in studies of the synthesis of ammonia from pure nitrogen-hydrogen mixtures. Great interest therefore attaches to studies of the synthesis of ammonia with the use of gas mixtures containing inert gases - methane and argon.

The influence of inert gases on the synthesis of ammonia was studied under 300 atm pressure, at 475, 500, and 525° and space velocities 30,000, 45,000, and 60,000 m³/m³ catalyst · hour.

EXPERIMENTAL METHOD AND DISCUSSION OF RESULTS

The investigations were performed in a large-scale laboratory unit, by a circulation method (Fig. 1). The nitrogen-hydrogen mixture was made by decomposition of ammonia followed by purification at atmospheric pressure. The inert gas was measured into the nitrogen-hydrogen mixture from a gas holder 0.5 m³ in capacity. Methane from the Melitopol' source and argon from the Sverdlovsk oxygen plant were used. Oxygen was removed from the methane and argon before use. The gas mixture was compressed to 300 atm and then fed into the apparatus. Purification of the fresh and recycled gas to remove oil and moisture was

*This paper reports part of the dissertation research work of N. A. Gavria.

effected by means of oil separators of the compressor and circulation pump, and by filters containing activated charcoal, silica gel, fused caustic, and cotton wool. The synthesis column was packed with 100 cc of industrial-type catalyst of medium activity. The composition of the catalyst was (in %): FeO 27.25, Al_2O_3 4.51, K_2O 2.25, CaO 0.24, SiO_2 0.1. The catalyst was reduced in pure nitrogen-hydrogen mixture at 300 atm and 500°. The column was internally heated. The maximum temperature difference along the catalyst layer was 10°. The condenser for the synthesis mixture was a coil immersed in a thermostat. A double-action pump was used for the circulation. The space velocity was measured by a high-pressure flow meter with an induction indicator of special design. At the start of each experiment the catalyst activity was checked for pure nitrogen-hydrogen mixture under the test conditions: 300 atm, 500°, and 30,000 m^3/m^3 catalyst-hour. When the activity corresponded to the value for the previous experiment, methane or argon was introduced into the gas mixture. Up to 30% of methane was introduced into the circulating mixture.

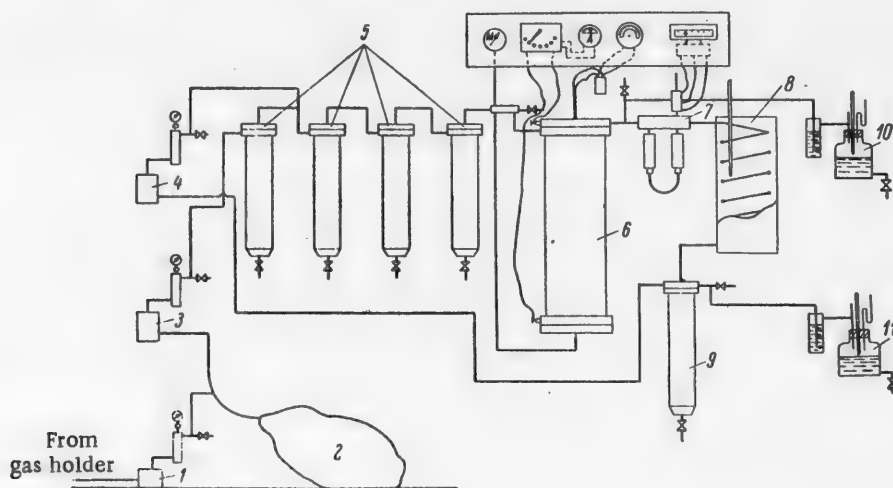


Fig. 1. Experimental unit. 1) Pump; 2) rubber gas holder; 3) compressor; 4) circulating pump; 5) filters; 6) synthesis column; 7) high-pressure flow meter; 8) condenser; 9) separator; 10, 11) aspirators.

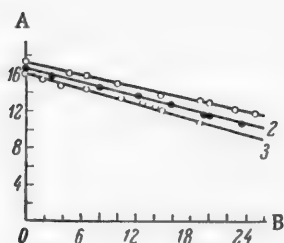


Fig. 2. Effect of methane content of the circulation mixture on the ammonia content of the converted gas. Pressure 300 atm, space velocity 30,000 hour^{-1} . A) Ammonia content (%), B) methane content (%). Temperature (°C): 1) 475; 2) 500; 3) 525.

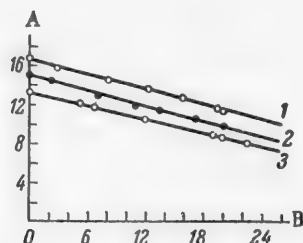


Fig. 3. Effect of methane content of the circulation mixture on the ammonia content of the converted gas. Pressure 300 atm, temperature 500°. A) Ammonia content (%), B) methane content (%). Space velocity (hour^{-1}): 1) 30,000, 2) 45,000, 3) 60,000.

TABLE 1

Ammonia Contents (%) in the Converted Gas with Different Contents (%) of Methane and Argon in the Circulation Mixture. Pressure 300 atm

Space velocity (m ³ /m ³ catalyst · hour)											
30000								45000		60000	
475°		500°		500°		525°		500°		500°	
CH ₄	NH ₃	CH ₄	NH ₃	A	NH ₃	CH ₄	NH ₃	CH ₄	NH ₃	CH ₄	NH ₃
0	17.2	0	16.7	0	16.9	0	16.05	0	15.0	0	13.2
4.78	16.5	2.86	15.8	2.47	15.9	1.91	15.4	2.39	14.3	5.27	12.11
6.75	15.8	8.1	14.55	5.65	15.5	3.8	14.75	7.21	12.88	6.7	11.85
10.0	15.0	12.3	13.65	9.13	14.7	6.66	14.25	11.0	11.95	11.99	10.5
14.78	13.8	15.86	12.8	15.8	13.0	10.48	13.5	13.4	11.5	19.0	9.05
18.95	13.2	19.4	11.7	19.6	11.6	12.78	13.0	17.25	10.69	20.01	8.85
22.8	12.25	23.6	10.75	—	—	14.2	12.67	20.1	10.0	22.5	8.26
—	—	25.6	10.35	—	—	14.85	12.15	—	—	—	—
—	—	27.4	9.82	—	—	15.15	11.7	—	—	—	—
—	—	28.3	9.65	—	—	18.93	10.9	—	—	—	—

The gas emerging from the column, and the circulating gas, were analyzed every 2 hours for ammonia and inert gas contents. Ammonia was determined by means of absorption bottles containing 0.1 N H₂SO₄ solution, and aspirators (Fig. 1). Methane was determined in the VTI gas-analysis apparatus. In experiments with argon, the gas mixture from the aspirator was passed over hot copper oxide. The hydrogen was burned, and argon and nitrogen were determined by the molecular-weight method.

TABLE 2

Values of the Coefficient a in Equation (1)

Space velocity (m ³ /m ³ catalyst · hour)	Coefficient a at temperature (°C)		
	475	500	525
30000	0.23	0.26	0.27
45000	—	0.25	—
60000	—	0.22	—

The use of the circulation method made it possible to increase smoothly the inert-gas content in the cycle, and to determine the relationship between the ammonia content in the converted gas and the inert gas in the circulation mixture at a given temperature and space velocity, in a single experiment.

The results of the experiments are given in Table 1 and Figs. 2 and 3.

The experimental data show that equal contents of methane and argon respectively in the circulation mixture have almost the same effect on the ammonia-synthesis process. The ammonia content of the converted gas decreases in proportion to the increasing content of methane or argon in the circulation mixture.

The relative decrease of the ammonia content of the converted gas is somewhat lower at 475° than at 500 or 525°. Thus, the ammonia contents in the gas mixture after the synthesis column, with 20% of methane in the circulation gas, as percentages of the ammonia content of the converted gas obtained when pure nitrogen-hydrogen mixture is used, are 73.6% at 475°, 68.6% at 500°, and 66% at 525°.

It follows from Table 1 and Fig. 2 that the ammonia content of the converted gas decreases in proportion to the increase of the methane content of the circulation mixture at all the space velocities studied.

Figures 2 and 3 show that the relationships between the ammonia content of the converted gas and the inert gas content of the circulation mixture are linear, and can be represented by the equation

$$x = x_0 - ai, \quad (1)$$

where x is the ammonia content of the converted gas (in %), x_0 is the ammonia content of the converted gas with the use of pure nitrogen-hydrogen mixture (in %), i is the inert-gas content of the circulation mixture (in %), and a is a coefficient the values of which are given in Table 2.

TABLE 3

Relative Yield of Ammonia, and Data for its Calculation

CH ₄ content in circulation mixture (%)	Actual yield (%)	Equili- brium yield	Actual yield	
			Equilibrium yield	
				$P = 360(1-i)^2$
0	16.7	26.44	0.63	300
2	16.2	25.6	0.63	288
4	15.7	24.8	0.63	276
6	15.14	24.0	0.63	265
8	14.62	23.2	0.63	254
10	14.1	22.4	0.63	243
12	13.58	21.62	0.628	232
14	13.06	20.8	0.628	222
16	12.55	20.0	0.627	211
18	12.02	19.3	0.625	202
20	11.5	18.5	0.624	192

Further, it follows that the relative yield of ammonia remains constant for the range of methane concentrations studied, if the equilibrium content of ammonia is calculated by means of Toniolo's equation [1] (Table 3). It follows from Table 3 that the relative yield decreases at high methane contents. With 30% methane in the circulation mixture, the relative yield decreases by 5%.*

For determination of the influence of the inert gas on the rate of the process, we used the kinetic equation of Temkin and Pyzhev [6, 7]

$$k = P^{0.5} v_z (1+z) I(z), \quad (2)$$

where z is the mole fraction of the newly formed ammonia, P is the pressure, and v_z is the space velocity at the exit from the column,

$$I(z) = - \frac{(1-z)^4}{2} \ln \left[1 - \frac{z^2}{L^2 (1-z)^4} \right],$$

where

$$L = \frac{z_{\text{equilibrium}}}{(1-z_{\text{equilibrium}})^3}.$$

Values of the rate constants calculated from Equation (2) are given in Table 4.

It follows from the data in Table 4 that at any given temperature the rate constant retains approximately the same value with variations of the methane content of the circulation mixture.

The experimental data were used to calculate the effectiveness at the catalyst with 0, 5, 10, 15, 20%

*As in original - Publisher's note.

methane in the circulation mixture. The results are plotted in Figs. 4 and 5. These graphs show that the productivity per 1 m³ of catalyst decreases in proportion to the inert gas content of the circulation mixture, the decrease being greater at higher space velocities.

TABLE 4

Rate Constants $k \cdot 10^4$ for Ammonia Synthesis, Pressure 300 atm

Temperature (°C)	Space velocity (m ³ /m ³ catalyst · hour)	k · 10 ⁴ at different % content of CH ₄ in the circulation mixture				
		0	5	10	15	20
475	30000	1.425	1.623	1.664	1.677	1.517
500	30000	2.041	2.298	2.114	2.035	2.161
525	30000	3.243	3.058	3.131	2.710	—
500	45000	2.412	2.330	2.210	2.078	2.031
500	60000	2.106	2.175	2.00	2.083	1.992

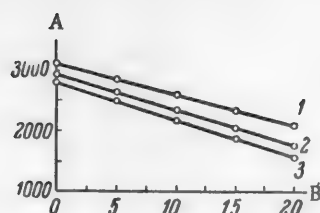


Fig. 4. Effect of methane content in the circulation mixture on the productivity per 1 m³ of catalyst. Pressure 300 atm, space velocity 30,000 hour⁻¹. A) Productivity (kg/hour), B) methane content (%). Temperature (°C): 1) 475; 2) 500; 3) 525.

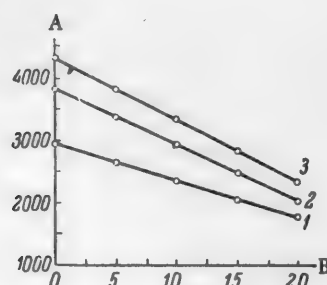


Fig. 5. Effect of methane content in the circulation mixture on the productivity per 1 m³ of catalyst. Pressure 300 atm, temperature 500°. A) Productivity (kg/hour), B) methane content (%). Space velocity (hour⁻¹): 1) 30,000; 2) 45,000; 3) 60,000.

It must be pointed out that despite the decrease of productivity with accumulation of inert gases in the circulation mixture, it is economically advantageous to carry out the process under such conditions.

SUMMARY

1. The influence of methane and argon on the synthesis of ammonia at 300 atm pressure, 475, 500, 525°, and space velocities 30,000, 45,000, 60,000 m³/m³ catalyst · hour was studied; it was found that the ammonia content of the converted gas decreases linearly with the inert-gas content of the circulation mixture at all temperatures and space velocities studied.

2. Coefficients have been determined whereby it is possible to calculate the ammonia contents of the gas mixture at the exit from the column in presence of inert gases in the circulation mixture.

3. It is shown that the reaction rate constants calculated from the Temkin-Pyzhev kinetic equation [6, 7] remain unchanged over the entire range of methane contents in the circulation mixture studied.

4. The productivity per 1 m³ of catalyst at different methane contents in the circulation mixture has been determined; it was found that the decrease of productivity with accumulation of inert gases is greater at higher space velocities.

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THE COUNTERCURRENT DIFFUSION OF KOH AND K_2CO_3 IN SOLID ADJACENT LAYERS OF KOH AND K_2CO_3 IN ABSORPTION OF WATER VAPOR BY THESE LAYERS

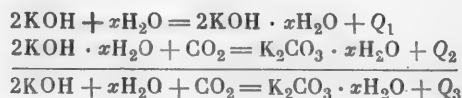
M. I. Kliashtornyi

In heterogeneous reactions proceeding with formation of a film of the reaction products, the rate of the process depends on a number of consecutive stages. The main determining steps of the process are the diffusion of the reacting gas through the layer of the spent material, and the chemical reaction.

Kinetic equations for such processes are based on the assumption that the zone of the reaction between the absorbent and the reacting gases begins at the boundary between the active absorbent and the spent material [1, 3]. The reaction may proceed within the solid absorbent, or in a thin layer, according to the physical properties of the absorbent.

However, there are processes in which a film of spent product is formed, to which the above kinetic scheme is not applicable. This is the case, for example, in the absorption of a mixture of gaseous CO_2 and H_2O by solid caustic potash.

The chemistry of the interaction of CO_2 and H_2O with solid KOH may be represented in general form by the following equations:



The specific features of this heterogeneous reaction are that two gaseous components, H_2O and CO_2 , react with the caustic potash, and that both the starting substance and the reaction product, KOH and K_2CO_3 , are readily soluble in water.

This may lead to countercurrent diffusion of KOH from the inner zones and of K_2CO_3 into the sorbent. This is particularly prominent if the stoichiometric ratio breaks down in diffusion. For example, if the flow rates of CO_2 and H_2O are nonequivalent, and, say, the amount of water diffusing is above the stoichiometric proportion, the role of the KOH concentration gradient becomes appreciable, leading to countercurrent diffusion.

As a result of the diffusion of alkali from the inner to the outer zones of the sorbent, the zone of reaction between the CO_2 and alkali is not directly at the surface of the active substance, but is displaced nearer to the outside, according to the sorption conditions (Fig. 1).

Naturally, with this process mechanism it cannot be said that the zone of reaction between the sorbent and the reacting gases begins at the interface between the active sorbent and the spent substance.

Consequently, countercurrent diffusion of the active and spent sorbent, to whatever extent it occurs, may alter the kinetic scheme of the process considerably.

The mechanism postulated for the absorption of CO_2 and H_2O by solid KOH is confirmed by the results of this investigation.

EXPERIMENTAL METHODS

The mechanism of the sorption of CO_2 and H_2O by solid KOH , with excess of water vapor in the gas phase, is clearly revealed by studies of the countercurrent diffusion of the active and spent sorbent. It is sufficient for the purpose to keep a specimen of solid active absorbent, KOH , covered with a layer of spent absorbent, K_2CO_3 , in a moist atmosphere and to analyze the active and spent sorbent layers at definite intervals.

Specimens in the form of plates were prepared for this purpose, of the following compositions: 1) powdered caustic potash, 0-0.25 mm fraction, 85%, fibrous asbestos 15%; and 2) powdered K_2CO_3 , 0-0.25 mm fraction, 80%, fibrous asbestos 10%.

Plates of the first composition were pressed at 300 kg/cm^2 in the form of three layers separated by gauze interlinings. These caustic plates were pressed together with plates of the second composition, also consisting of three layers, at 45 kg/cm^2 . The weight of a layer in plates of both compositions was 20 g.

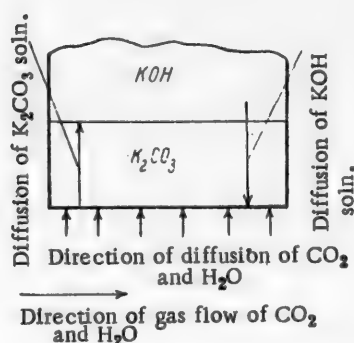


Fig. 1. Kinetic scheme of the process.

The prepared plates were fitted into a rectangular iron tray 1, $120 \times 55 \times 60 \text{ mm}$ and held down by an aluminum frame with the aid of a clamp bolt (Fig. 2).

The fitted tray was placed in a chamber containing saturated water vapor. The experiments were continued for 24, 36, and 72 hours at $25-27^\circ$. The following external changes were noted during dismantling of the trays: 1) water diffused through three layers of the carbonate plates in all the experiments; 2) layer I of the caustic plate consisted of small amounts of caustic and a layer of fibrous asbestos after experiments lasting 24 and 36 hours; no solid caustic was found after 72 hours; 3) crystalline potassium carbonate was found at the interface between layers I and II (Fig. 2) of the carbonate plates. After the tray had been dismantled, each layer of the plates was analyzed for K_2CO_3 and KOH by Warder's method.

The results of the experiments are shown in the diagrams (Figs. 3-7).

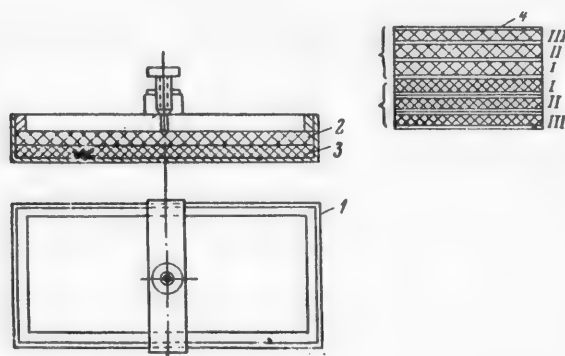


Fig. 2. Tray with the test specimens. 1) Iron tray; 2) carbonate plate; 3) caustic plate; 4) gauze interlining; I, II, and III) layers.

DISCUSSION OF RESULTS

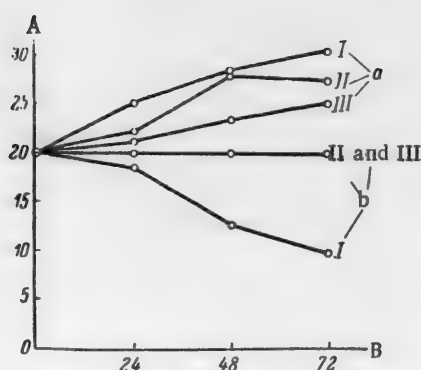


Fig. 3. Weight variations of the layers in the carbonate and caustic plates. A) Weight of layer (g), B) time (hours). a) layers of carbonate plate; b) layers of caustic plate.

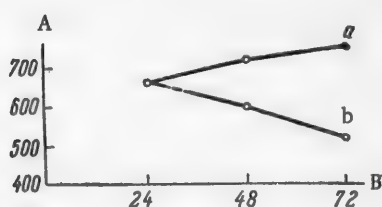


Fig. 4. Variations of alkalinity in the plates. A) Total alkalinity in plate (in ml of 1 N HCl), B) time (hours). Plates: a) carbonate; b) caustic.

K_2CO_3	2.08	2.5	4.45	9.56	16.4	21.13	28.21	34.39	47.03	49.32	53.27
KOH	55.11	53.77	47.01	37.53	30.82	25.97	19.9	14.61	4.48	2.35	0
Composition of solid phase	K_2CO_3	K_2CO_3	K_2CO_3	K_2CO_3	K_2CO_3	K_2CO_3	K_2CO_3	K_2CO_3	K_2CO_3	K_2CO_3	K_2CO_3
	KOH	KOH	KOH	KOH	KOH	KOH	KOH	KOH	KOH	KOH	KOH
	$K_2CO_3 \cdot 1\frac{1}{2} H_2O$										

It is clear that when concentrated solutions of K_2CO_3 and KOH meet (mix), the less soluble K_2CO_3 is precipitated.

Under these conditions the K_2CO_3 concentration in the saturated solution is low, about 2.5 wt. %.

This accounts for the high carbonate concentration in layer II of the carbonate plate (Fig. 6). Consequently, beyond this boundary zone the substance diffusing into the material consists almost entirely of water. It also accounts for the fact that almost nothing but asbestos was found within the caustic plate.

The explanation of the peculiar course of the curve for layer III of the carbonate plate (Fig. 7) is that carbonate diffuses rapidly at first. The amount of carbonate lost is not compensated by the caustic diffusing inward.

The weight variations of the layers in the carbonate and caustic plates are plotted in Fig. 3. It is seen that layers II and III of the caustic plates did not change in weight during the experiment. Layer I of the caustic plate lost over 50% of its caustic by the end of the experiment. The caustic lost from layer I of the caustic plate diffuses into the carbonate plates; this is confirmed by the graph in Fig. 4.

The KOH concentration in the layers of the carbonate plate decreases from layer I to layer III (Fig. 5).

These experimental results indicate that the moisture, on reaching the caustic, dissolves it. The concentrated KOH solution formed diffuses outward, counter-current to the carbonate solution.

The fall of carbonate concentration from layer III to layer I, from the outside inward, is shown in Fig. 3. This graph indicates that the moisture moves mainly by diffusion of carbonate solution (in the form of moving films of saturated solution), which results in transfer of carbonate. If the moisture moved into the material in vapor form, the carbonate concentration would not decrease from the plate surface toward the inner layers.

The explanation for the formation of crystals at the boundary between layers I and II is that carbonate is salted out from the saturated carbonate solution diffusing inward, by the action of KOH diffusing in the opposite direction.

The joint solubility of K_2CO_3 and KOH at 30° (in wt. %) is given below [4]:

SUMMARY

The countercurrent diffusion of KOH and K_2CO_3 was studied, and it was shown that an active sorbent may diffuse into the outer zones. This indicates that processes are possible in which the reaction zone is not directly at the surface of the active substance, but is closer to the outside, according to the sorption conditions.

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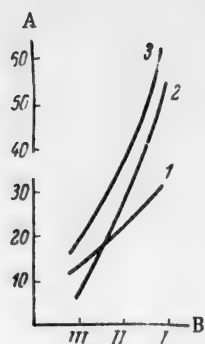


Fig. 5. Variations of the KOH concentration in different layers of the carbonate plate. A) KOH concentration (in ml of 1 N HCl); B) layers. Duration of experiment (hours): 1) 24; 2) 48; 3) 72.

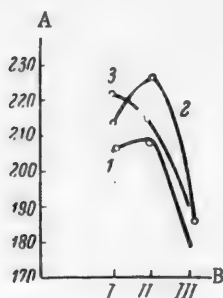


Fig. 6. Variations of carbonate concentration in different layers of the carbonate plate. A) Carbonate concentration (in ml of 1 N HCl), B) layers. Duration of experiment (hours): 1) 24; 2) 48; 3) 72.

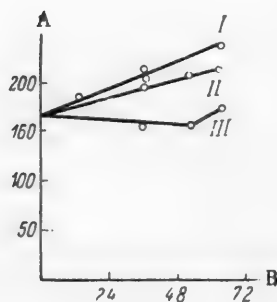


Fig. 7. Variations of alkalinity in the carbonate plate. A) Total alkalinity (in ml of 1 N HCl); B) time (hours). I, II, III) layers of carbonate plate.

*In Russian.

THE DYNAMICS OF A SUSPENDED LAYER OF LIQUID IN A GAS

I. P. Mukhlenov

(The Leningrad Technological Institute, Leningrad)

A suspended layer of liquid in a gas, in the form of mobile foam, is formed in sieve equipment, by virtue of the kinetic energy of the gas when it is passed upward through a grid and a layer of liquid on it, at linear velocities above 1 m/second. The suspended layer of mobile foam is a highly turbulent gas-liquid system consisting of rapidly moving bubbles and streams of gas, closely intermingled with films and streams of liquid.

A mobile foam ensures rapid heat and mass transfer between gas and liquid, with a very extensive phase contact area and low diffusion resistance; therefore the foam process for the treatment of gases and liquids proved more effective than earlier methods in a number of industries.

The height H of the layer of mobile foam (or the volume fraction of gas in the foam) determines the reaction volume in which the gas and liquid interact, and hence the operating rate of the equipment. Therefore one of the principal problems of the hydrodynamics of suspended layers is the determination of the height H of the suspended layer, together with calculation of the hydraulic resistance of the layer. It is convenient, for calculation purposes, to use the dimensionless specific height of the foam layer, H_{sp} , which is numerically equal to the specific volume of the foam.

$$H_{sp} = \frac{H}{h_0} = \frac{v_b}{v_l} = \frac{\gamma_l}{\gamma_b} \quad (1)$$

* The following notation is used in this paper:

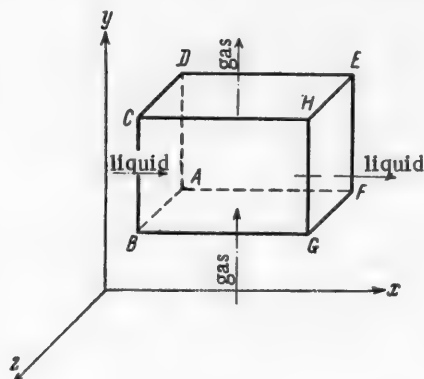
A , the coefficient in the equation; a_f , the width (height) of the overflow orifice (in m); b , the width of the grid (in m); b_f , the length of the overflow weir (overflow orifice) (in m); D_e , the equivalent diameter of the apparatus (in m); d_0 , the diameter of the orifice (in m); d_b , the diameter of a bubble (in m); g , the acceleration due to gravity; H , the height of the foam layer (in m); H_p , the height of the foam layer above the center of the overflow orifice, the pressure head (in m); h_0 , the height of the original layer of liquid on the grid (in m); l , the length of the grid (in m); m , distance between orifice centers (in m); P , the total pressure of liquid (or gas); $\Delta P_1(P_g)$, the pressure drop, hydraulic resistance; S_f , the area of the overflow orifice (in m²); v , the specific volume (in m³/kg) or volume (in m³); $w_{g,l}$, the linear velocity (of gas or liquid) in the apparatus (in m/second); x, y, z , the projections of the vector on the corresponding axes; $\gamma = \rho g$, the specific gravity (in kg/m³); μ , the dynamic coefficient of viscosity (in kg/second · m² or kg/hour · m²); $\nu = \frac{\mu}{\rho}$, the kinematic coefficient of viscosity (in m²/second or m²/hour); ρ , the density (in kg · second²/m⁴); σ , the coefficient of surface tension (in kg/m); τ , the time in the foam layer (seconds); $\varphi_{g,l}$ the volume fraction (of gas or liquid) in the foam; $\Gamma_1 = \frac{D_e}{h_0}$, criterion representing the ratio of the height to the length of the liquid layer; $\Gamma_2 = \frac{m}{d_0}$, criterion representing the open section of the grid; $\Gamma_3 = \frac{H_p b}{S_f}$, the overflow criterion, representing the pressure of the

[footnote continued next page]

The character of mobile foam and the physical conditions for its existence are described in a series of papers on foaming interaction of gases and liquids [1-3].

In this paper the kinematics and dynamics of a suspended layer of mobile foam are formulated; this is followed by derivation of a general criterial equation describing the hydrodynamics of the foam layer, which provides the basis for analysis of experimental data in order to derive calculation formulas.

In sieve equipment with overflow weirs, operated under mobile foam conditions (foam apparatus), complex interaction of the gas and liquid takes place. The gas moves upward, while the liquid moves along the grid in cross flow to the gas. The forward movements of the gas and liquid are accompanied by turbulent pulsations greatly varying in extent and velocity, with individual streams and bubbles of gas and drops of liquid taking a great variety of directions. However, the velocity of the turbulent pulsations is a function of the forward velocity of the gas, and may be expressed in terms of the latter.



Motion of gas and liquid in an elemental volume of foam.

The kinematics and dynamics of gas and liquid streams in a foam layer were considered in detail [4] with the use of the known method whereby an elementary parallelepiped is isolated in the foam layer, and the motion of the gas and liquid in this parallelepiped analyzed as shown in the Figure. The following equations were derived for isothermal motion in nonsteady conditions when the influence of mass transfer on the height and the resistance of the foam layer is negligible:

a) equation for the continuity of flow of gas passing through the foam layer

$$\frac{\partial (\rho_g v_{gx} w_{gx})}{\partial x} + \frac{\partial (\rho_g v_{gy} w_{gy})}{\partial y} + \frac{\partial (\rho_g v_{gz} w_{gz})}{\partial z} + \frac{\partial (\rho_g v_g)}{\partial \tau} = 0 \quad (2)$$

or in vector form;

$$\frac{\partial (\rho_g v_g)}{\partial \tau} + \text{div} (\rho_g v_g w_g) = 0, \quad (2a)$$

where

$$v_g = 1 - \frac{h_0}{H}; \quad (3)$$

* [continued from previous page]

mobile foam at the overflow orifice; $Re_g = \frac{w_g D_e}{\nu_g}$, the Reynolds criterion for the gas in the cross section of the apparatus, determining the degree of turbulence of the foam layer; $Re_1 = \frac{w_1 h_0}{\nu_1}$, the Reynolds criterion

for the liquid flowing along the grid; $Ho = \frac{w\tau}{h_0}$ the homochronicity criterion, characterizing unsteady motion in the foam layer; $Eu = \frac{\Delta p g}{\gamma w^2}$, the Euler criterion, characterizing the ratio of the pressure drop in the foam

layer to the kinetic energy of the gas (or liquid); $Fr = \frac{w^2}{gh_0}$, the Froude criterion, characterizing the ratio of the inertia forces in the gas (or liquid) to its weight; $We = \frac{\sigma}{\gamma_1 \cdot h_0^2}$ the Weber criterion; H_{sp} , the specific height of the foam, representing the increase in the suspended liquid layer relative to the original height.

Subscripts: g - gas, 1 - liquid, b - bubble, f - overflow, overflow orifice.

b) equation for the continuity of flow of the liquid along the grid in the foam layer:

$$\frac{\partial \varphi_1}{\partial \tau} + \frac{\partial (\varphi_1 w_{1,x})}{\partial x} + \frac{\partial (\varphi_1 w_{1,y})}{\partial y} + \frac{\partial (\varphi_1 w_{1,z})}{\partial z} = 0 \quad (4)$$

or in vector form:

$$\frac{\partial \varphi_1}{\partial \tau} + \operatorname{div} (\varphi_1 \mathbf{w}_1) = 0, \quad (4a)$$

where

$$\varphi_1 = \frac{h_0}{H}. \quad (5)$$

It follows from the form of Equations (2) and (4) that they differ from the continuity equations for pure one-phase streams [5] by the presence of the factor $\varphi_{g,l}$:

c) equation of motion for the liquid:

$$\frac{\partial \mathbf{w}_1}{\partial \tau} + (\mathbf{w}_1, \operatorname{grad}) \mathbf{w}_1 = -\nu_1 \operatorname{rot. rot} \mathbf{w}_1 - \frac{1}{\rho_1} \operatorname{grad} P_1 - \mathbf{g}; \quad (6)$$

d) equation of motion for the gas:

$$\frac{\partial \mathbf{w}_g}{\partial \tau} + (\mathbf{w}_g, \operatorname{grad}) \mathbf{w}_g = \nu_g (1/3 \operatorname{grad. div} \mathbf{w}_g - \operatorname{rot. rot.} \mathbf{w}_g) - \frac{1}{\rho_g} \operatorname{grad} P_g - \mathbf{g}. \quad (7)$$

The dynamic Equations (6) and (7) were obtained in the form of typical Navier-Stokes equations, and therefore they are given here only in the vector form, which is more compact than the coordinate form. It should be noted that in the derivation of the equations of motion by the law of momentum in the projections on the coordinate axes each term of the equation contained a term of the form:

$$\left(\varphi_1 + \frac{\partial \varphi_1}{\partial x} dx \right) dv,$$

which cancelled out on algebraical addition of the terms. The result was typical Navier-Stokes equations.

The system of differential equations (2a-7) is connected by boundary conditions, which were determined by analysis of the literature data on the influence of various parameters in relation to foam layers.

It is known [6, 7] that the following conditions should hold in a gas-liquid system at the gas-liquid interface:

a) equality of the frictional forces:

$$\nu_g \operatorname{grad} \mathbf{w}_g = \nu_1 \operatorname{grad} \mathbf{w}_1, \quad (8)$$

b) equality of pressures and surface tension:

$$P_g = P_1 + 4 \frac{\sigma}{d_b}. \quad (9)$$

The hydrodynamics of the foam layer may be influenced by various geometrical (design) parameters. It was found in some studies of bubbling conditions in sieve equipment [8-10] that in the experimental conditions in question the diameter of the apparatus, D_{app} , or its ratio to the height of the liquid layer in the grid, h_0 , influence the hydrodynamics of the process. Others, however [11, 12] have given detailed proofs that the hydrodynamics of the bubbling process is independent of the diameter of the equipment.

For investigation of this question in relation to a foam layer under otherwise constant conditions, we formulated the following condition:

$$H_{sp} = A_1 \left(\frac{D_e}{h_0} \right)^p. \quad (10)$$

In accordance with published data [9, 13, 14], the influence of the orifice diameter d_0 and the distance m between the centers of the orifices under constant operating conditions is determined by the equation

$$H_{sp} = A_2 \left(\frac{m}{d_0} \right)^q. \quad (11)$$

In nonequilibrium motion (at the starting of the apparatus, with flow of liquid through the grid orifices and spray in the gas), the specific height of the gas-liquid layer may vary along the length l or the width b of the grid; this may be formulated as

$$H_{sp} = f \left(\frac{l}{b} \right). \quad (12)$$

In the operation of equipment with augmented foam pressure [4], to maintain a constant height H of foam on the grid, the velocities of the foam along the grid w_b and in the overflow orifice w_{bf} must be in a definite ratio, inversely proportional to the stream cross section

$$\frac{w_{bf}}{w_b} = \frac{Hb}{S_f} = \frac{Hb}{a_f b_f} \quad (12a)$$

Since $\frac{w_{bf}}{w_b} = \frac{w_f}{w_1}$, Equation (12a) may be written

$$\frac{w_f}{w_1} = \frac{Hb}{S_f} = \frac{Hb}{a_f b_f}. \quad (13)$$

Here w_1 and w_f are the fictitious velocities of the liquid on the grid and in the overflow orifice. The value of the foam height H in Equation (13) may be replaced by a quantity proportional to it, H_p , which represents the height of the foam stream necessary for foam to flow through the overflow orifice.

Equations (2-13) are insufficient for analytical solution of the problem for a number of reasons, and primarily because the number of unknowns is greater than the number of equations. These equations could be used for determination of the functional relationships between the parameters in question by the method of similarity.

By scale transformations [6] of the equations of motions and boundary conditions (2-13), a general criterion equation for hydrodynamic similarity of the foam layer was derived:

$$F_1 \left(Ho_1, Ho_g, Re_1, Re_g, Eu_1, Eu_g, Fr_1, Fr_g, We, \right. \\ \left. \frac{\Delta P_g h_0}{\sigma}, \frac{H}{h_0}, \frac{v_g}{v_1}, \frac{w_1}{w_g}, \frac{D_e}{h_0}, \frac{m}{d_0}, \frac{l}{b}, \frac{H_p b}{S_f} \right) = 0. \quad (14)$$

For technical calculations in planning and operation of foam equipment, the general criterial Equation (14) was simplified [4] by elimination of the criteria Ho_1 , Ho_g and $1/b$, which characterize nonequilibrium motion, and combination of certain criteria with transformation of criteria of one type into another. No parameters determining the formation of a suspended layer of mobile foam were eliminated in the transformations; this was confirmed during subsequent practical application of the equations obtained.

The transformations yielded the following equations, describing the operation of foam equipment under steady conditions:

a) for determination of the height of a suspended layer of mobile foam:

$$\frac{H}{h_0} = F_2 \left(Re_g, Re_1, We, \frac{\gamma_g}{\gamma_l}, \Gamma_1, \Gamma_2, \Gamma_3 \right); \quad (15)$$

b) for determination of the hydraulic resistance of a tray:

$$Eu_g = F_3 \left(Re_g, Re_1, We, \frac{\gamma_g}{\gamma_l}, \Gamma_1, \Gamma_2, \Gamma_3 \right). \quad (16)$$

SUMMARY

1. A general criterial Equation (14) for hydrodynamic similarity of a foam layer was derived by means of scale transformations of equations of motion and boundary conditions.

2. Working formulas for determination of the specific height of a foam layer (15) and the hydraulic resistance of a tray (16) were derived by simplification and transformation of the general equation.

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ELECTRICAL CONDUCTANCE OF SALTS IN THE FUSED STATE

V. A. Kochinashvili and V. P. Barzakovskii

In fused salt baths which are widely used for the heat treatment of nonferrous and ferrous metal articles in the range between 200 and 1350°, the fused salt itself acts as the heated resistance [1-3].

The electrical conductivities of the fused salts used must be accurately known for efficient utilization of the furnaces and for their design. However, no data are available in the literature on the conductivities of a number of fused salts and mixtures of salts used in fused salt baths. For example, the system barium chloride - calcium chloride, used in the 750-950° range, has not been studied.

This paper presents data on the conductivity of barium chloride (up to 1300°) and the binary system barium chloride - calcium chloride in the 700-1100° range.

EXPERIMENTAL METHODS

Method for the measurement of electrical conductivities of fused salts. An improved four-arm alternating-current bridge [4-7], the circuit diagram of which is given in Fig. 1, was used for measurements of the melt conductivities. The bridge was supplied from a sonic-frequency tube generator (TG), with variable frequency between 20 and 20,000 cps.

The null instrument (NI) was an electron-beam oscillograph type EO-4, with an input amplifier with a high amplification factor. It was therefore connected in the circuit without an additional tube amplifier.

The EO-4 oscillograph, which can be used with current of almost any frequency, is considerably better and more sensitive than the telephone generally used in previous investigations. With the use of the oscillograph it was possible to analyze the influence of frequency on the results. Moreover, it was possible to observe, on the oscillograph screen, distortions of the potential sinusoid of the measuring diagonal of the bridge under the influence of the polarization capacity of the measurement cell, capacitive coupling between the leads and ground, external electromagnetic and electrostatic fields, etc.; this was of considerable help in accurate balancing of the bridge.

To minimize the potential drop in the connecting leads, all the connections were copper leads 2 mm in diameter, and the number of leads was kept as small as possible.

All the sections of the bridge were shielded, to eliminate electrostatic interaction between the individual sections and the influence of external fields.

To compensate for the polarization capacity of the measurement cell, a variable capacitor C_1 was connected in parallel with the resistance box R. To decrease the polarization effect, the platinum disks used as electrodes were coated with a layer of platinum black, and had a rough surface after heating.

The funnel-shaped cell used for the conductivity measurements, shown in Fig. 2, was made from transparent quartz glass. The cell had a capillary about 1.2 mm in internal diameter. The cell constant was of the order of 304 cm⁻¹. The cell, and especially the capillary, became a dull white after the determinations, but the cell was attacked very little, as the cell constant, which was checked after each experiment, varied only very slightly.

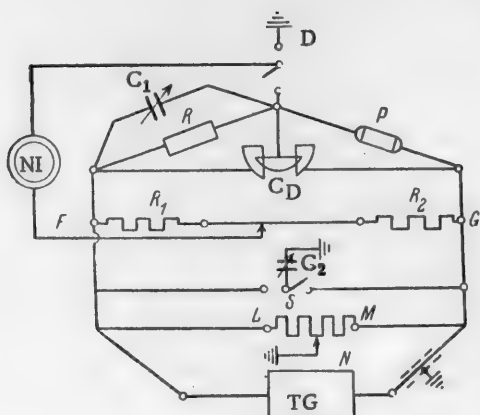


Fig. 1. Bridge circuit. R) Nonreactive plug resistance box type MShB, error not exceeding $\pm 0.5\%$; P) conductivity cell; C_1) capacitor box, 100 millimicrofarads to 1 microfarad; C_D) differential capacitor up to 450 cm capacity; R_1, R_2) supplementary coils for increasing the length of the slide wire up to 10 meters; LM) rheochord of supplementary grounding bridge; C_2) variable capacitor up to 500 millimicrofarads; S) two-way switch for connecting the capacitor C_2 in parallel with the rheochord LM on either side of the slider.

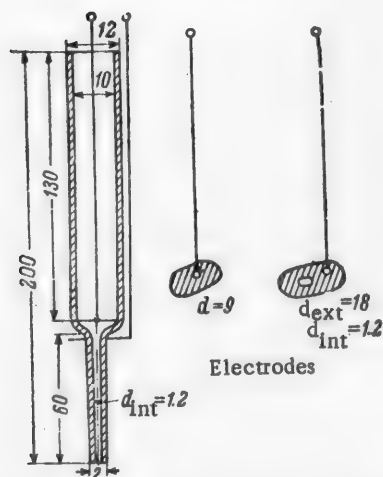


Fig. 2. Cell for measurements of conductivity of fused salts. Dimensions in mm.

* As in original - Publisher's note.

The measurement cell was immersed in a test tube with the fused salt. The temperature was measured by means of a platinum/platinum-rhodium thermocouple which was immersed in the test tube containing the fused salt. The e.m.f. of the thermocouple was determined by means of the PP-II laboratory potentiometer, the temperature being measured to $\pm 0.5\%$ accuracy.

An electric furnace with Silite rods was used for fusing the salt and keeping it in the fused state. A temperature of 1300° was attained relatively easily.

The furnace temperature was regulated by variations of the current strength by means of a variable resistance, and was maintained for only 3-5 minutes. The melt in the cell quickly reached the furnace temperature, and this time was quite sufficient to reach a constant temperature in the layer of melt and to carry out the measurements.

The following procedure was used for balancing the bridge in the determinations.

1) A resistance of the box R close to the resistance of the cell was chosen, and the position of the slider on the wire FG was found at which the null instrument showed that the bridge was balanced. However, the minimum was spread over 4-5 cm of the wire.

2) To find a sharper minimum, a capacity C_1 (capacitor box) was connected parallel to the resistance box R. The capacity was so chosen that the minimum on the slide wire was within 1 cm; it must be noted that the differential capacitor C_D could be connected either to the measurement cell or to the resistance box R, which considerably improved the bridge balancing conditions.

3) The bridge balance was improved by means of a supplementary grounding bridge, which brought the terminals of the null instrument to ground potential. For this, one terminal of the null instrument was grounded by means of the switch D, and the balance position of the bridge was found by movement of the slider N along the rheochord LM.

The bridge balance was improved by inclusion of the capacitor C_2 . This gave the sharpest balance, as it was obtained in conditions in which the bridge had purely ohmic resistances.

4) After the supplementary bridge had been balanced, the circuit was switched over to the main bridge and the final balance in it was found.

The required resistance R_x was calculated from the formula

$$R_x = R_b \frac{l_1}{l_2},$$

where R_b is the resistance of the box, and l_1 and l_2 are the corresponding lengths of the wire arms. The measurements were performed with three different values of R_b , and the average value was taken. The conductivity of the melt was calculated by means of the formula $\kappa = \frac{c}{R_x}$, where c is the cell constant, and R_x is the active resistance of the melt determined by the bridge method.

The cell constant $c = \frac{1}{S}$ was determined at the beginning of the experiment with the use of standard potassium chloride solutions. It was impossible to find it by calculation, as exact calculation of the ratio $1/S$ for the cell, which was of irregular shape, was not possible.

In determinations of the cell constant the frequency was varied from 500 to 20,000 cps, and to compensate for the polarization capacity of the cell a variable capacity C_1 was connected in parallel with the resistance box. The results of the measurements are given in Table 1.

TABLE 1

Variations of Cell Constant with the Capacity in Parallel with the Resistance Box, and the Frequency

Con. std. KCl soln. (in g KCl/1000 g H ₂ O)	Resistance R_1 (ohms). Capa- city C_1 (mmf). Cell constant c (cm ⁻¹)	Frequency (kilocycles/second)				
		0.5	1	2	5	20
76.6276 (at 18°)	R_1	3130	3130	3130	3120	3100
	C_1	3000	2800	2700	2500	2200
	c	306	306	306	305	303
76.6276 (at 25°)	R_1	2750	2750	2750	2730	2660
	C_1	3400	3200	3000	2700	2400
	c	305	305	305	304.6	302
7.4789 (at 18°)	R_1	27350	27350	27350	27300	27100
	C_1	2500	2400	2300	2100	1800
	c	305.5	305.5	305.5	304	302.5

From the data in Table 1, the cell constant was taken as 304 cm⁻¹.

The following conclusions can be drawn from Table 1 concerning the influence of frequency on the determination results: 1) frequency variations between 500 and 2000 cps have almost no influence on the bridge balance or the cell constant; 2) at 5000 cps the bridge balance is appreciably affected and the cell constant is altered by 0.5%; 3) at 20000 cps the cell constant is changed by 1.5%, which is quite considerable.

The conductivity measurements of the fused salts were carried out at 1000 cps.

TABLE 2

Conductivity of Barium Chloride

Tempera- ture (°C)	Conductivity κ (ohm ⁻¹ · cm ⁻¹)
1000	2.042
1050	2.208
1100	2.347
1150	2.432
1200	2.574
1250	2.631
1300	2.752

To balance the bridge, the values of the capacity connected in parallel with the resistance box to compensate for the polarization capacity of the cell must be varied according to the electrolyte. Experiments with aqueous potassium chloride solutions and fused salts showed that: 1) the compensating capacity C_1 depends on the nature and magnitude of the resistance being measured; for example, in measurements of the conductivity of potassium chloride solutions (Table 1), C_1 is 3400-1800 mmf and its value increases with concentration of the aqueous solution; in measurements of conductivity of fused salts in quartz vessels C_1 reaches 0.52-0.62 μ f; 2) the compensating capacity increases with decreasing frequency (Table 1); 3) the compensating

capacity C_1 also depends on the design of the measurement cell; whereas small capacities (0.52-0.62 μ f) must be used in experiments with a quartz cell and capillary, it was shown by one of us [8] that in determinations with platinum cells fairly large capacities, of the order of 10-15 μ f, are required.

Conductivity of the system CaCl_2 - BaCl_2 . Literature data on the conductivity of BaCl_2 are confined to 1100°, whereas fused salt baths are used at temperatures up to 1300°. We therefore investigated the conductivity of pure barium chloride up to 1300°. The results are given in Table 2.

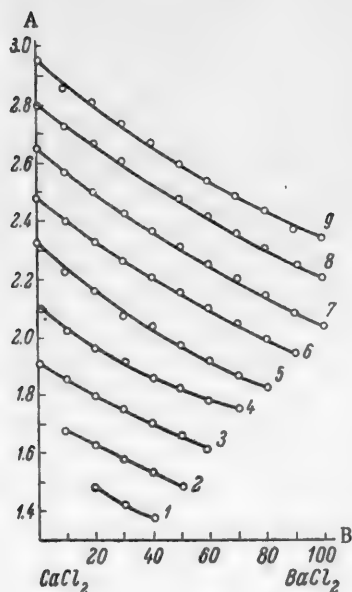


Fig. 3. Conductivity isotherms for the system calcium chloride - barium chloride. A) Conductivity (in $\text{ohms}^{-1} \cdot \text{cm}^{-1}$); B) composition (molar %): Temperature (°C): 1) 700, 2) 750, 3) 800, 4) 850, 5) 900, 6) 950, 7) 1000, 8) 1050, 9) 1100.

It follows from the data in Table 2 that the conductivity of barium chloride increases by about 30% between 1000 and 1300°. Therefore the current in the fused salt bath increases considerably with increase of temperature from 1000 to 1300°; this is confirmed in practice.

The conductivity of the binary system barium chloride - calcium chloride was studied in the 700-1100° region (Table 3).

The conductivity isotherms for this system, plotted in Fig. 3, show appreciable deviations from the straight lines joining the values for the pure components, in the direction of lower conductivities. The conductivity-temperature relationship is not linear. The conductivity increase slows down at higher temperatures. This behavior is typical of fused salts [9].

The operating current of a fused salt bath directly depends on the conductivity of the fused salt. We carried out special experiments with the S-45 fused-salt furnace, with barium chloride as the fused salt. It was found that the operating current increases from 3200 to 4500 amps with increase of temperature from 1000 to 1300°.

The 1.4-fold increase of current approximately corresponds to the increase in the conductivity of barium chloride from 1000 to 1300°:

$$\frac{2.752}{2.042} = 1.347.$$

TABLE 3

Conductivity of the System Barium Chloride - Calcium Chloride

CaCl_2 content (molar %)	Conductivity ($\text{ohms}^{-1} \cdot \text{cm}^{-1}$) at temperature (°C)								
	700	750	800	850	900	950	1000	1050	1100
0	—	—	—	—	—	—	2.04	2.21	2.35
10	—	—	—	—	—	1.96	2.09	2.27	2.39
20	—	—	—	—	1.82	2.01	2.14	2.31	2.44
30	—	—	—	1.76	1.87	2.05	2.21	2.35	2.51
40	—	—	1.62	1.79	1.93	2.1	2.27	2.42	2.56
50	—	1.49	1.65	1.82	1.98	2.17	2.32	2.49	2.60
60	1.39	1.53	1.71	1.87	2.05	2.22	2.38	2.54	2.66
70	1.43	1.58	1.76	1.92	2.08	2.27	2.44	2.61	2.74
80	1.49	1.63	1.80	1.98	2.15	2.33	2.51	2.67	2.81
90	—	1.69	1.84	2.02	2.23	2.39	2.57	2.72	2.86
100	—	—	1.91	2.10	2.32	2.48	2.65	2.79	2.94

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DYNAMICS OF CHEMISORPTION IN BUBBLING TOWERS

V. B. Fal'kovskii, Iu. I. Mel'nikov, and A. V. Vetrova

(The M. V. Lomonosov Institute of Fine Chemical Technology, Moscow)

The dynamics of the chemical processes occurring between liquid and gas phases in bubbling towers has been studied little [1], although it is of considerable interest. Bubbling towers can be used for continuous processes, and the heat of reaction can be easily removed. Catalysts can be held in suspension by the action of small bubbles in liquid layers, and processes can be accelerated as the result of formation of large interfaces by the action of small bubbles.

The present investigation deals with the influence of the dimensions of bubbling towers and gas rates on the degree of absorption of olefins in the alkylation of liquid benzene by ethylene and propylene in presence of 5 wt. % of anhydrous aluminum chloride at 80° under atmospheric pressure, and in the polymerization of isobutylene bubbled through a layer of 87% sulfuric acid at 100° under atmospheric pressure. The dynamics of the absorption of atmospheric oxygen bubbled through a layer of liquid n-butyraldehyde in presence of 0.1 wt. % of manganese acetate at 13±3° under atmospheric pressure was also studied.

Ethylene, propylene, and isobutylene were prepared by dehydration of ethyl, isopropyl, and isobutyl alcohols respectively, over aluminum oxide in a quartz tube 30 mm in diameter, placed in a horizontal electric furnace with automatic temperature control.

Uniform supply of alcohol vapor into the furnace was effected by means of an evaporator with an internal electric heater consisting of a Nichrome spiral, the current in which was regulated by means of a variable resistance and measured with a ammeter. The evaporator was insulated on the outside to reduce heat losses. The space velocity of the olefin at constant temperature in the contact zone and constant current strength in the evaporator heater was determined by preliminary calibration.

The olefins obtained by dehydration of the alcohols were separated from water and unreacted alcohols in a water condenser, and then passed through three consecutive columns, each 30 mm in diameter and 350 mm high, filled with granulated alumina previously heated at 250°, to remove water and alcohol vapors. Isobutylene was dried over granulated anhydrous calcium chloride.

The dried olefins were fed into the bubbling tower to be investigated, at constant rates from 400 to 1200 cc/minute. The olefins not absorbed in the bubbler were measured in a constant-pressure gas holder.

Empty glass cylindrical towers 20, 30 and 50 mm in diameter and with bubbling layers from 30 to 480 mm high were tested. A glass disk with 10-15 holes 1 mm in diameter was inserted in the bottom of the tower to produce numerous bubbles of 7-10 mm initial size. For the alkylation and polymerization reactions, the towers were immersed in an electrically heated water thermostat. The temperature within the towers was measured by means of a mercury thermometer.

In the alkylation of benzene, the volume of the original ethylene decreased between 1.8 and 6-fold, and the volume of the propylene between 7 and 130-fold, depending on the height of the bubbling layer and the olefin rate.

In the polymerization of isobutylene, its volume decreased from 4.3 to 49-fold, according to conditions.

Experiments were also carried out on the polymerization of isobutylene diluted with methane. A mixture of isobutylene and methane was first made in a gas holder, and it was then fed through drying columns into the bubbler containing 87% sulfuric acid heated to 100°. The initial isobutylene concentration was 10-50%; after the reaction the isobutylene concentration fell to 3%.

The experiments showed that the rate of irreversible chemisorption processes in bubbling towers may be represented by the equation [2]:

$$\frac{H}{s} = \frac{w_1}{k}, \quad (1)$$

where H is the height of the bubbling layer (in m); $w_1 = \frac{V_1}{\rho}$ (in $\text{m}^3/\text{m}^2 \cdot \text{hour}$) is the initial gas rate for the full cross section of the tower, ρ , (in m^3); $s = \ln \frac{y_1}{y_f}$ where y_1 and y_f are the volume concentrations of the reacting component in the gas at the entry and exit of the tower respectively (in vol. %). For concentrated gases, $s = \ln \frac{V_1}{V_f}$, where V_1 and V_f are the volume velocities of the reacting gas at entry and exit of the bubbling layer respectively (in m^3/hour); k is the volume coefficient of chemisorption (in $\text{m}^3/\text{m}^3 \cdot \text{hour}$) at atmospheric pressure.

By analogy with other mass-transfer processes [1, 3], $\frac{H}{s}$ may be termed the height equivalent to a reactor unit, or the height of the bubbling layer in which the concentration or partial volume of the reacting gas decreases by a factor of $e = 2.71828$. The dimensionless quantity s , the number of reactor units, is a measure of the degree of conversion.

The height equivalent to a reactor unit increases relatively little with increase of the gas rate for the given chemisorption process; to determine the value of $\frac{H}{s}$ it is not necessary to know the phase contact area, which is very difficult to determine in bubbling reactors. However, the initial bubble size should be given, as it influences the height of the equivalent reactor unit [2].

The results were plotted in log-log coordinates. It is seen that the degree of absorption of olefins increases with increasing height of the bubbling layer and with decreasing gas rate.

For the alkylation of benzene by propylene, the values of $\frac{H}{s}$ were 20-40 mm for initial propylene rates from 23 to 240 $\text{cc}/\text{cm}^2 \cdot \text{minute}$ respectively. For the alkylation of benzene by ethylene, the values of $\frac{H}{s}$ were 200-490 mm for initial propylene rates from 43 to 480 $\text{cc}/\text{cm}^2 \cdot \text{minute}$ respectively. For the polymerization of isobutylene, the values of $\frac{H}{s}$ were 80-110 mm for initial isobutylene rates from 50 to 240 $\text{cc}/\text{cm}^2 \cdot \text{minute}$ respectively.

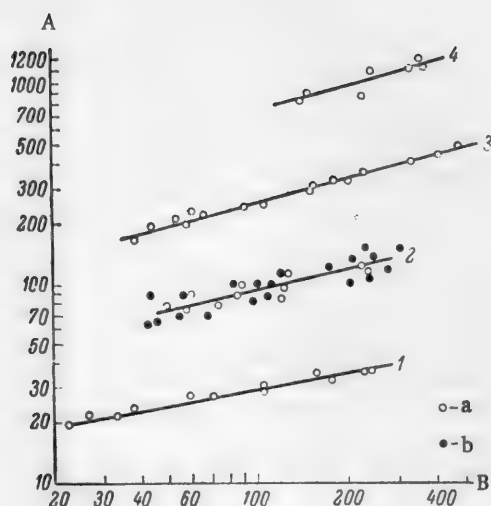
Dilution of isobutylene by methane does not significantly change the values of the height equivalent to a reactor unit found for concentrated isobutylene. If the bubbling layer has a height equivalent to the reactor unit, then at a constant initial rate of the gas mixture the isobutylene concentration decreases 2.71828-fold, irrespective of the initial isobutylene concentration; this is characteristic of first-order reactions.

The influence of catalyst poisoning on the chemisorption rate was not studied.

The reaction products obtained in the alkylation of benzene with olefins, and in the polymerization of isobutylene, were isolated by known methods.

The oxidation of butyraldehyde by air was carried out in similar towers, 500 mm high, provided with water jackets for maintaining the temperature at $13 \pm 3^\circ$ in the bubbling layer. Running water at $4-5^\circ$ was fed into the jacket.

The air used for oxidation was measured by means of a rheometer and a gas meter and dried over granulated alumina in three consecutive columns each 30 mm in diameter and 350 mm high. The air volume rate was regulated by means of a water-jet pump. The butyraldehyde vapor carried over by the exit gas from the bubblers was collected in traps with solid carbon dioxide.



Effect of initial gas rate on the height equivalent to a reactor unit. A) H/s ratio (in mm), B) initial gas rate for the full section of the column, w_1 (in $\text{cc}/\text{cm}^2 \cdot \text{minute}$). 1) Alkylation of benzene by propylene; 2) isomerization of isobutylene; a) isobutylene, b) mixture of isobutylene and methane; 3) alkylation of benzene by ethylene; 4) oxidation of butyraldehyde by air.

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The oxygen concentration in the exit gas fell to 10-18% depending on the height of the bubbling layer and the air rate. The concentration of butyric acid in the reaction product reached up to 96 wt. % (depending on the experimental conditions) in 2-4 hours. From 1 to 3% of perbutyric acid was present in the reaction mixture during the reaction.

The acid content of the reaction mixture was determined by titration with alkali in presence of phenolphthalein, and the per-acid content was found iodometrically.

The exit gas was analyzed in the Orsat apparatus. The exit gas usually contained 0.5-1% carbon dioxide. The oxygen balance was calculated for each experiment.

The results of these experiments (see Figure) show that Equation (1) is also applicable to the oxidation of butyraldehyde by air. When the initial air rate is increased from 140 to 340 $\text{cc}/\text{cm}^2 \cdot \text{minute}$, the values of $\frac{H}{s}$ increase from 700 to 1000 mm.

The rate of absorption of atmospheric oxygen by butyraldehyde does not depend on the concentrations of aldehyde and butyric acid in the reaction mixture. The slight decrease of the chemisorption rate observed at the end of the reaction is probably due to poisoning of the catalyst.

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THE KINETICS OF THE RECTIFICATION PROCESS

R. S. Fraiman

Determination of the duration of the start-up period is necessary in the distillation of mixtures in which the relative volatility is close to unity. For example, in Huffman and Urey's experiments [1] on the production of water enriched with O^{18} isotope and deuterium, material equilibrium in the column was established only after 300 hours.

The solution proposed by these authors, and also by Brodskii and Skarre [2], to the question of the length of the start-up period is based on the following assumptions:

1) It is assumed that after thermal equilibrium has become established in the column not all the plates of the column take part in the rectification process, but only the lowest plates at first. Gradually, as equilibrium conditions are approached, an increasing number of plates takes part in the rectification until finally, at the instant when equilibrium is established, the whole column comes into operation. This assumption is represented schematically for columns on open cycle in Fig. 1. In packed rectification columns, the whole packing is wet with the liquid at the initial concentration, and both the lower and the upper regions of the column take part in the rectification.

2) It is considered that, during the start-up period, transfer of the light fraction along the column remains constant and equal to the product of the amount of incoming mixture and the difference of the contents of the low-boiling component in the vapor and liquid. The same assumption was made by Coulson [3], who investigated the time required to attain equilibrium in laboratory packed columns.

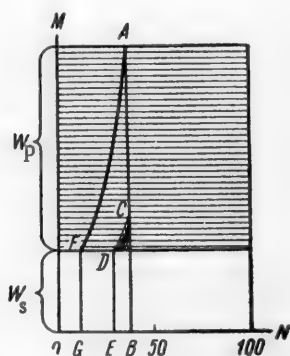


Fig. 1. Distribution of the low-boiling component over the plates and in the still for a column on open cycle at various stages of the start-up period. M) Amount of liquid in the still and on the plates of the column, N) contents of low-boiling component (%). AB represents the initial composition, ACDE is the distribution of concentrations at an intermediate instant of the start-up period, AFG represents the distribution of concentrations at the instant when equilibrium is reached.

However, if a constant concentration difference always exists between the vapor ascending in the column and the falling liquid, equilibrium in the column cannot be attained, as owing to this difference the high-boiling component will accumulate in the still indefinitely. At the initial stages after the start a ratio determined by the Raoult or Henry laws may exist between the concentrations of the low-boiling component in the vapor and liquid, but as the column approaches equilibrium this ratio breaks down, and the vapor and liquid concentrations become equal at the instant when equilibrium is attained.

Let us consider the following case: 1) the column operates under adiabatic conditions; 2) at the initial instant the concentrations of liquid in the still and on the plates are equal; 3) the mixture obeys Raoult's law.

The loss of the low-boiling component from a rectification column on open cycle at the initial instant of the start-up period can be calculated from the following formula:

$$v(y_1 - x_1) = v \cdot x_1 \frac{(\epsilon_0 - 1)(1 - x_1)}{1 - (\epsilon_0 - 1) \cdot x_1}, \quad (1)$$

where \underline{y} is the amount of original liquid fed to the top plate of the column (in moles/hour); x_1 is the concentration of the low-boiling component in the original liquid; y_1 is the concentration of the low-boiling component in the vapor over the top plate; ϵ is the relative volatility.

At the instant when equilibrium is reached, the vapor and liquid concentrations become equal, $y_1 = x_1$, and the loss of the low-boiling component becomes $v(y_1 - x_1) = 0$.

In a rectification column operating under equilibrium conditions, the liquid concentration on any plate of the column, x_2 (a plate in this case means a region of the column containing a liquid of definite concentration) and the liquid concentration at the top plate, x_1 , are related by the following expression, valid at infinite reflux ratio:

$$\frac{x_2}{1-x_2} : \frac{x_1}{1-x_1} = \epsilon^n \quad (2)$$

Solving this equation for x_2 , we find the concentration distribution along the column at the instant when equilibrium is established. However, at the beginning of the start-up period the concentration is the same on all the plates, and only gradually alters with time. Thus, at the first instant the efficiency of the whole column does not exceed the efficiency of one theoretical plate, despite the fact that the vapor passes along the whole column; in other words, $n = 1$ in Equation (2). It is therefore possible to introduce a new variable, η , the coefficient of deviation of the system from the equilibrium state. The coefficient η , and therefore $\epsilon = \epsilon_0^\eta$, change in value with time. At the initial moment of distillation the nominal relative volatility is $\epsilon_0^{\frac{1}{n}}$, where $\eta = \frac{1}{n}$ and then the efficiency of the whole column, equivalent to \underline{n} theoretical plates is $\epsilon_0^{\eta n} = \epsilon_0^{\frac{1}{n} \cdot n} = \epsilon_0^1$, or only one theoretical plate. At the instant when equilibrium is established, when $\eta = 1$, the efficiency of the whole column becomes $\epsilon_0^{1 \cdot n} = \epsilon_0^n$ or \underline{n} theoretical plates.

Using the coefficient η and the expression $\epsilon = \epsilon_0^\eta$ from Equation (2), we find the law for the distribution of the concentrations over the plates (along the height of the column) at any instant of the start-up period.

$$x_2 = \frac{\frac{x_1}{1-x_1} \epsilon_0^{\eta n}}{1 + \frac{x_1}{1-x_1} \epsilon_0^{\eta n}} \quad (3)$$

At some intermediate instant the amount \underline{L} of the low-boiling component in the system can be calculated as the sum of the amounts of the low-boiling component in the still and on the plates. The average concentration x_{av} of the low-boiling component on the plates can be determined at high values of \underline{n} , on the assumption that the concentration varies smoothly from plate to plate, by integration of Equation (3) with respect to \underline{n} . The value found for the average concentration in the column is used to determine the amount of the low-boiling component at some instant before equilibrium is reached:

$$L = w_s \frac{x_1 \cdot \epsilon_0^{\eta n}}{(1-x_1) + \epsilon_0^{\eta n} \cdot x_1} + w_p \cdot \frac{1}{n} \frac{\ln[(1-x_1) + x_1 \cdot \epsilon_0^{\eta n}]}{\ln \epsilon_0^{\eta n}} \quad (4)$$

where w_s is the amount of liquid in the still, and w_p is the amount of liquid on the plates.

It is evident that during time dt , with a feed rate \underline{y} moles/hour, the amount of low-boiling component removed from the system is dL , and the removal of the low-boiling component occurs owing to concentration difference between the vapor leaving the top plate and the liquid entering the top plate:

$$dL = v(y - x_1) dt \quad (5)$$

The amount of low-boiling component removed from the column varies with time, with variations of the concentration y of the low-boiling component in the vapor phase, and it also depends on the variations, in time, of the amount of the low-boiling component on the plates.

For solution of Equation (5), Equation (4) is differentiated with respect to the variable which changes with time, i.e., η ; y is expressed in terms of x by Raoult's law with the nominal relative volatility $\epsilon = \epsilon_0^\eta$; the time differential dt is isolated and the integration is performed.

The result, after transformation, gives:

$$\begin{aligned} t = & \frac{w_s}{v} n \ln \epsilon_0 \int_{\frac{1}{n}}^1 \frac{\epsilon_0^{\eta} [1 + x_1 (\epsilon_0^{\eta} - 1)]}{[(1 - x_1) + x_1 \epsilon_0^{\eta}]^2 \cdot (\epsilon_0^{\eta} - 1)} d\eta + \\ & + \frac{w_p}{v} \frac{1}{(1 - x_1)} \int_{\frac{1}{n}}^1 \frac{\epsilon_0^{\eta} [1 + x_1 (\epsilon_0^{\eta} - 1)]}{[(1 - x_1) + x_1 \epsilon_0^{\eta}] \cdot (\epsilon_0^{\eta} - 1)} d\eta - \\ & - \frac{w_p}{v \cdot n} \int_{\frac{1}{n}}^1 \frac{[1 + (\epsilon_0^{\eta} - 1) x_1] \ln [(1 - x_1) + x_1 \epsilon_0^{\eta}]}{\ln \epsilon_0 \cdot x_1 (1 - x_1) \eta^2 (\epsilon_0^{\eta} - 1)} d\eta. \end{aligned} \quad (6)$$

Unfortunately, direct integration of this equation involves difficulties, as the primary function for the three integrals in it cannot be determined by simple methods. However, since the integrands are fairly simple and the quantities contained in them are of the same type, integrals of Equation (6) can be easily found by calculation with variation of the variable η from $\frac{1}{n}$ to 1.

In usual distillation processes, especially in batch rectification, the original mixture is put in the still, where the high-boiling component accumulates. During the distillation, the low-boiling liquid gradually displaces the high-boiling component from the plates. The higher the plate above the column, the greater is the enrichment with the low-boiling component. Distillation of this type is represented schematically in the same coordinate system in Fig. 2.

Let us assume for the sake of simplicity that the amount of liquid in the still greatly exceeds the amount of liquid held up in the column. In that case accumulation of the low-boiling component on the plates or in the packing does not affect the composition of the liquid in the still; its concentration is x_2 at the start, and remains the same at equilibrium.

The composition x_D of the liquid at the top of the column, and the average concentration x_{av} , vary while equilibrium is becoming established. For determination of these values we assume, as before, that $\epsilon_0^\eta = \epsilon$ and make use of the ratio (2), but expressed in terms of x_2 , which is constant in this case.

As a result we find:

$$x_D = \frac{\epsilon^n \cdot x_2}{\epsilon^n \cdot x_2 + 1 - x_2}. \quad (7)$$

With an infinitely large still, the concentration y_2 of the vapor entering the column remains unchanged during the start-up period, but the concentration of the falling liquid alters. If at the initial instant the falling liquid is in equilibrium with the rising vapor, then at the instant equilibrium is reached $y_2 = x$.

By Raoult's law, we can write for any time instant

$$x = \frac{\epsilon x_2}{(1 - x_2) + \epsilon x_2} = \frac{\epsilon_0^\eta \cdot x_2}{(1 - x_2) + \epsilon_0^\eta \cdot x_2}. \quad (8)$$

The amount of low-boiling component removed from the still is:

$$v(y_2 - x) = v \left\{ \frac{\varepsilon_0 x_2}{\varepsilon_0 x_2 + (1 - x_2)} - \frac{\varepsilon_0^{\eta} \cdot x_2}{\varepsilon_0^{\eta} x_2 + (1 - x_2)} \right\} =$$

$$= v \cdot \frac{x_2(1 - x_2)(\varepsilon - \varepsilon_0^{\eta})}{[\varepsilon_0 x_2 + (1 - x_2)] \cdot [\varepsilon_0^{\eta} x_2 + (1 - x_2)]} \quad (9)$$

Using a formula analogous to Equation (5), we find the time required to reach equilibrium:

$$t = \frac{w_p}{v} \int_{\frac{1}{n}}^1 \frac{[\varepsilon_0 x_2 + (1 - x_2)] \cdot [\varepsilon_0^{\eta} x_2 + (1 - x_2)] \cdot \varepsilon_0^{\eta}}{(1 - x_2) \cdot \eta \cdot [\varepsilon_0 - \varepsilon_0^{\eta}] \cdot [\varepsilon_0^{\eta} \cdot x_2 + (1 - x_2)]} d\eta -$$

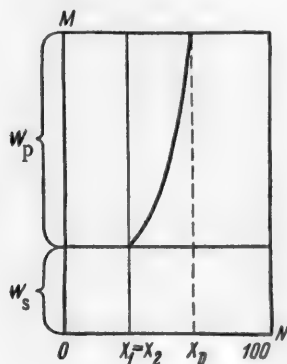
$$- \frac{w_p}{v} \int_{\frac{1}{n}}^1 \frac{[\varepsilon_0 x_2 + (1 - x_2)] \cdot [\varepsilon_0^{\eta} x_2 + (1 - x_2)] \cdot \ln [\varepsilon_0^{\eta} x_2 + (1 - x_2)]}{n \cdot \ln [\varepsilon_0 \cdot x_2 (1 - x_2)] \cdot \eta^2 (\varepsilon_0 - \varepsilon_0^{\eta})} d\eta. \quad (10)$$

Equation (10) can be solved by calculation, as direct integration is difficult. It is valid for columns with a large amount of liquid in the still.

In laboratory practice it is often necessary to separate a small quantity of a mixture containing substances of similar boiling points. In such cases the amount of liquid in the still of the rectification column is not large, and variations of its composition should have a significant influence on the time required to reach equilibrium. Let us consider rectification with a limited amount of liquid in the still (Fig. 3). In this case the amount of low-boiling component accumulating on the plates corresponds to the loss of the low-boiling component from the still (it is assumed that during establishment of the equilibrium state the column operates at infinite reflux ratio). The total amount of low-boiling component in the whole system still + column remains the same. Therefore the following equation is valid for any instant after the start of distillation:

$$w_p \cdot x_1 + w_s \cdot x_1 = w_p \cdot x_{av} + w_s \cdot x_2 = \text{const.} \quad (11)$$

Fig. 2. Schematic distribution of concentration in a column on closed cycle when $w_s \gg w_p$. M) Amount of liquid in the still and on the plates, N) content of low-boiling component (in %).



In this instance the concentration x_2 is not constant; until equilibrium is established it depends on the time from the start of the process, and on the parameters of the system, i.e., the amounts of liquid in the still and on the plates, the properties of the mixture, number of plates, etc. Equation (11) can be used to find the average composition of the liquid on the plates

$$x_{av} = \frac{w_p x_1 + w_s \cdot x_1}{w_p} - \frac{w_s x_2}{w_p} \quad (12)$$

It is seen that the average composition of the liquid on the plates is a linear function of the composition of the liquid in the still. To obtain an expression connecting the initial concentration of the liquid in the still and its concentration during the period when equilibrium is being established, we equate the expression obtained by integration, with respect to \underline{n} , of a relationship analogous to (3) for determination of the average concentration, to Equation (12):

$$\frac{1}{n} \frac{\ln [x_2 \cdot \epsilon^n + (1 - x_2)]}{\ln \epsilon} = \frac{w_p \cdot x_1 + w_s \cdot x_1}{w_p} - \frac{w_s \cdot x_2}{w_p} \quad (13)$$

Unfortunately, x_2 cannot be found in explicit form, and Equation (13) must be solved graphically. Since ϵ^n can be replaced by ϵ_0^{η} , where $\eta = \varphi(t)$, Equation (13) gives the course of the variation of concentration of the liquid in the still with time. At the instant when equilibrium is attained, when $\eta = 1$, Equation (13) can be used to determine the concentration of the liquid in the still and, with the aid of Equation (2), the concentration of the distillate.

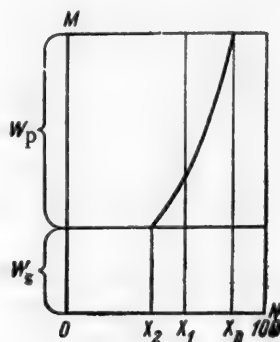


Fig. 3. Schematic distribution of concentrations in a column on closed cycle for comparable values of w_s and w_p . M) Amount of liquid in the still and on the plates, N) content of low-boiling component (%).

To determine the time required to reach equilibrium, we must find the differential of the accumulation of the low-boiling component in the system with respect to time. However, it follows from Equation (11) that the amount of low-boiling component remains constant in the system still + column, i.e., the differential is zero. Therefore, to determine the time required to reach equilibrium, we shall consider only part of the system; for example, the time required to reach equilibrium in the column apart from the still. It is clear that the time required to reach equilibrium in a part of the system is the same as in the whole system, as we cannot have a system with interrelated parts in which equilibrium is not reached simultaneously. Let us therefore consider the time required to reach equilibrium on the plates. We denote the amount of low-boiling component on the plates by L_p . We then substitute the value of x_{av} and obtain the second term in Equation (4); differentiation then gives formulas analogous to those derived earlier, but with the difference that x_2 is not constant, as was the case earlier, but varies with variations of η .

The rate of loss of the low-boiling component from the still, as before, is given by the difference $(y_2 - x)$, but in this instance both y_2 and x are variable. Therefore Equation (10) is also applicable to the case in question if it is taken into account that $x_2 = \varphi(\eta)$. This relationship is implicit in Equation (13).

Solution of this equation for x_2 must be carried out graphically for different values of η . The corresponding values of η and x_2 are then substituted into Equation (10). Equation (10) makes it possible to determine the time required to reach equilibrium in a rectification column.

Such calculations were performed for the mixture heptane-methylcyclohexane, for which $\epsilon_0 = 1.07$. The calculations were carried out for columns equivalent to 100 and 50 theoretical plates. The details of the packing and of the columns themselves, taken from Coulson's paper [3], are given in the Table.

The Table shows that Coulson's formula always gives low values for the time required to reach equilibrium. The reason is that he makes the entirely arbitrary assumption that the loss of low-boiling components from the still is constant. For the examples given in the Table, the time required to reach a state of the column such that $\eta = 0.99$ is considerably greater than that found by Coulson's formula [3].

If the height of the column is doubled, the start-up time is greatly increased. Decrease of the initial concentration from 0.5 to 0.1 results in an almost 20-fold increase of the time.

Decrease of the amount of liquid held up in the column shortens the period of nonequilibrium operation of the column.

Thus, the problem of the nonequilibrium operation of rectification column has been solved, and the solution is illustrated by examples.

Characteristics of the Columns Under Consideration

Column characteristics	Type of packing					
	Stedman packing, lens-shaped units	single-turn spirals 2.25 mm dia. from wire d = 0.3 mm	spiral grid	single-turn spirals 1.5 mm dia., from wire d = 0.34 mm	single-turn glass spirals 3 mm dia.	Podbielniak wire spirals d = 0.2 mm, 7 turns/inch
Diameter (cm)	2.5	2.54	1.7	2.54	1.0	0.45
Length (cm)	62.5	95	91.5	85	195	470
Height equivalent to 1 theoretical plate (cm)	1.25	1.9	1.83	1.7	3.9	9.4
Boiling rate v (cc/hour)	150	506	400	1013	157.1	159.1
Total holdup H (cc)	9.5	60	15	80	35	14.5
Still charge 20 H (cc)	190	1200	300	1600	700	290
H/v ratio	0.0638	0.1184	0.0375	0.079	0.2228	0.0911
Time to reach equilibrium (hours), by Coulson's formula for $n = 50$, $\epsilon_0 = 1.07$, $x_1 = 0.1$	3.1	5.8	1.8	3.9	10.9	4.5
By Formula (10) for $\left\{ \begin{array}{l} \eta = 0.99 \\ \eta = 0.8 \end{array} \right.$	21.8	40.7	12.9	28.0	78.0	82.3
$n = 50$, $\epsilon_0 = 1.07$, $x_1 = 0.1$	3.7	6.93	2.15	4.66	13.0	5.38

Columns of doubled height, equivalent to 100 theoretical plates, with the same boiling rate v but with double the amount of liquid in the column and still

Time to reach equilibrium (hours), by Coulson's formula for $n = 100$, $x_1 = 0.1$, $\Sigma_0 = 1.07$	11.4	21.3	6.8	14.2	40.2	16.4
By Formulas (10) and (13) for $\left\{ \begin{array}{l} \eta = 0.99 \\ \eta = 0.8 \end{array} \right.$	236.0 23.2	450.0 43.5	141.0 13.7	294.0 29.0	830.0 82.0	340.0 33.2
By Coulson's formula for $n = 100$, $x_1 = 0.1$	2.95	5.52	1.75	3.68	10.4	4.25
By Formulas (10) and (13) for $\left\{ \begin{array}{l} \eta = 0.99 \\ \eta = 0.8 \end{array} \right.$	10.0 5.5	18.7 10.3	5.95 3.26	12.5 6.86	85.3 19.4	14.45 7.94

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A POLAROGRAPHIC STUDY OF THE COPRECIPITATION OF NICKEL AND ZINC TOGETHER WITH ALUMINUM HYDROXIDE

P. N. Kovalenko

(State University, Rostov-on-Don)

It is extremely difficult to obtain pure precipitates of aluminum hydroxide in presence of accompanying substances, including nickel and zinc, because of adsorption effects on the surface of the amorphous $\text{Al}(\text{OH})_3$ precipitate.

Many bivalent cations, including zinc and nickel, are not precipitated by excess of ammonia from solutions of their pure salts. However, when aluminum is precipitated by ammonia in the form of the hydroxide, these cations are partially precipitated as the hydroxides along with it [1]. Such coprecipitation also occurs in presence of considerable excess of ammonium hydroxide; in such cases nickel and zinc amines are probably adsorbed, forming solid solutions. Therefore the quantitative separation of aluminum from zinc and nickel by the classic method is incomplete [1]. We invariably found ammonium ions together with zinc and nickel in precipitates of aluminum hydroxide washed thoroughly with hot water. A large excess of ammonium hydroxide largely prevented the coprecipitation of nickel and zinc, but a small amount of aluminum hydroxide dissolved in this excess of NH_4OH [2].

It has been shown by a number of workers [2-5] that the first stage in the formation of stable solids containing the principal component and impurities in precipitation is adsorption. We wished to find conditions in which impurities, including nickel and zinc, would not be precipitated to any practical extent, and aluminum hydroxide would not dissolve appreciably in the precipitant solution.

The theory and mechanism of adsorption effects have been discussed and described fully by Dumanskii [6], Dubinin [7], Frumkin [8], and others, and therefore they are not considered here.

The degree of adsorption of nickel and zinc by amorphous aluminum hydroxide precipitates was determined by means of the polarograph, the dropping-mercury electrode of which responds accurately and sensitively to changes of salt concentration in solution, by a decrease of the diffusion current [9-11].

The purpose of the present work was to demonstrate the applicability of the polarographic method to determinations of adsorption by freshly precipitated aluminum hydroxide, and to investigations of the adsorption isotherms of nickel and zinc ions. It was shown by us earlier [12, 13] that zinc and nickel can be determined polarographically in presence of aluminum salts by the method of additions.

EXPERIMENTAL METHODS

To study the influence of a number of factors on the adsorption of zinc and nickel by aluminum hydroxide, the adsorption of nickel and zinc ions in presence of ammonium chloride, and ammonia was investigated. A precipitate of $\text{Al}(\text{OH})_3$ was shaken with nickel or zinc solutions for 30-60 minutes, filtered, and dissolved in 30 ml of 2 N sulfuric acid solution with gentle warming. This solution, or filtrate, was transferred to a 100 ml measuring flask, followed by 2 g of KCNS or 2 g of $\text{C}_3\text{H}_4(\text{OH})(\text{COOH})_3$; the mixture was neutralized to $\text{pH} = 2$ if the solution contained nickel, and to $\text{pH} = 3$ in presence of zinc, and the liquid was made up to the mark with distilled water. Fifteen ml of this solution was placed in the cell, 2 drops of 1% phenyl red solution was added, and the polarographic determination was performed; the concentrations of the metals were determined from a calibration graph (Fig. 1) or by the method of additions (Fig. 2).

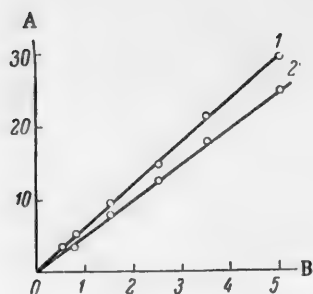


Fig. 1. Polarographic calibration graphs for nickel and zinc in presence of 0.1 N aluminum sulfate solution and 2% potassium thiocyanate solution. Solution temperature 22°. A) Diffusion current (microamps.), B) salt concentration (millimoles/liter). Calibration graphs: 1) zinc, 2) nickel.

The M-7-200 visual polarograph of the Institute of Chemistry, Gor'kii University, was used for the determinations; the mirror galvanometer used in the determinations had absolute sensitivity $3.2 \cdot 10^{-9}$ amps/mm/m, $R_{ext} = 200$ ohms, $R_{crit} = 400$ ohms, distance from mirror to scale 0.25 m. The voltage range was 0 to 2 v; the solution temperature was 20°. The wave height was measured by Hohn's method [14].

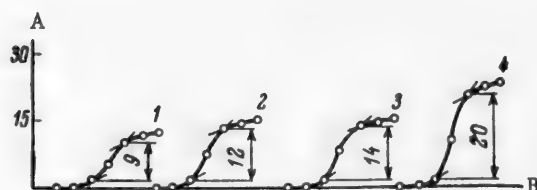


Fig. 2. Polarogram of zinc and nickel sulfates in presence of 0.1 N aluminum sulfate solution and 2% potassium thiocyanate solution. A) Height of diffusion wave (in mm), B) potential (in V). Curves: 1) Ni, 2) Ni + 0.003 g additive, 3) Zn, 4) Zn + 0.004 g additive.

action of ammonium ions is so high that in many cases the adsorption and coprecipitation of bivalent ions forming complex salts with ammonia can be reduced to a very low level. Therefore aluminum was precipitated by 5 ml of 20% ammonia (~ 12 moles/liter) in presence of 2.0 g of ammonium chloride (~ 0.37 moles/liter); the total volume of the solution was 100 ml. The precipitate was left to settle for 60 minutes, filtered, and analyzed for impurities.

Data on the influence of aluminum sulfate concentration on the coprecipitation of zinc and nickel are given in Fig. 3. It follows from the adsorption isotherms of nickel and zinc that in the region of low adsorbent concentrations the amounts of zinc and nickel adsorbed are relatively large, and the adsorption of zinc is greater than that of nickel. Zinc ions evidently have greater affinity for aluminum hydroxide than for nickel

Data on the influence of ammonium sulfate concentration on the reproducibility of the results are given in Table 1. These data show that the results of polarographic determinations of zinc and cobalt are satisfactorily accurate and reproducible.

Nickel and zinc, which are nobler elements than aluminum, can be determined polarographically in presence of salts of the latter [9] (Fig. 2).

The polarographic method for determination of low concentrations of ions adsorbed on amorphous precipitates of metal hydroxides has the advantage that the determination can be carried out without separation of the adsorbent if the ions of the latter are reduced at the dropping-mercury electrode at more negative potentials than the adsorbed ions. In this instance the half-wave potentials of simple salts of zinc, nickel, and aluminum are 1.06, 1.10, and 1.72 v respectively [14]. In some cases the nickel and zinc salts remaining in the filtrate were determined polarographically; the amounts of Zn and Ni adsorbed were then determined from the difference between their initial and final concentrations in the filtrate.

The effects of concentration of aluminum, nickel and zinc salts, solution pH, and concentrations of NH_4Cl and ammonia on the adsorption of zinc and nickel ions by aluminum hydroxide were studied.

For studies of the effect of the concentration of aluminum sulfate solution on the coprecipitation of nickel and zinc, the solutions of the latter had the same concentration, 0.005 mole/liter. Only the concentration of the aluminum salt was varied; from 0.01 to 0.2 mole/liter in precipitation in presence of nickel, and from 0.02 to 0.1 mole/liter in precipitation in presence of zinc.

The adsorption of extraneous ions is reduced considerably if the precipitant is a buffer solution consisting of excess ammonia and ammonium salts in high concentration. Under these conditions the substituting

ions. However, at higher concentrations of the aluminum salt the relative adsorption of both the metals decreases considerably, and tends to a constant value.

Because of its high dispersion, aluminum hydroxide has a high adsorptive power [15]. When ammonia is gradually added to solutions containing sulfates of aluminum, nickel, and zinc, at first (pH of medium ~4) anions are coprecipitated with $\text{Al}(\text{OH})_3$; on further addition of excess ammonia they are redissolved at a rate which depends on the solution pH. The higher the aluminum concentration in the solution, the more nickel and zinc ions are adsorbed by aluminum hydroxide.

TABLE 1

Effects of the Concentration of Aluminum Salt on the Sensitivity of the Polarographic Method, Accuracy, and Reproducibility of Determinations of Nickel and Zinc by the Addition Method (Total volume of solution used, 100 ml; adsorption time 30 minutes)

Taken (mg)		Added to solution (g)						Found by polarographic addition method (mg)					
Zn	Ni	$\text{Al}_2(\text{SO}_4)_3$	KCNS	$\text{C}_2\text{H}_5(\text{OH})(\text{COOH})_3$	NH_4Cl	25% NH_4OH solution (ml)	pH of solution	zinc			nickel		
								1st experiment	2nd experiment	3rd experiment	1st experiment	2nd experiment	3rd experiment
5.0	5.0	0.57	2.0	—	2.0	5.0	—	5.10	5.15	5.12	5.20	4.9	5.0
5.0	4.0	0.60	—	3.0	2.0	5.0	—	5.15	5.10	5.15	4.15	4.2	3.9
0.50	0.50	0.30	2.0	—	—	—	2.0	0.52	0.52	0.53	0.52	0.48	0.49
0.85	0.90	0.20	2.0	—	2.0	—	2.0	0.87	0.88	0.87	0.92	0.88	0.88
3.0	2.0	0.40	—	3.0	2.0	5.0	3.0	2.95	3.0	3.1	2.1	1.9	1.9
2.0	2.0	0.40	2.0	—	2.0	—	2.0	2.0	1.9	2.1	2.0	2.0	2.1
10.0	10.0	0.60	—	3.0	2.0	5.0	4.0	10.3	10.2	10.3	10.3	10.0	10.3
20.0	20.0	0.60	—	3.0	2.0	5.0	4.0	20.5	20.7	20.4	20.4	20.3	20.0

To determine the relationship between pH and the adsorption of zinc and nickel, the precipitation of aluminum sulfate from 0.1 molar solution in presence of 0.37 mole/liter of NH_4Cl and $5 \cdot 10^{-3}$ mole/liter of nickel and zinc sulfates was studied. Ammonia was used as the precipitant, and the solution volume was 100 ml; the pH was determined potentiometrically with the aid of the quinhydrone electrode up to pH 8, and with a hydrogen electrode above this value.

As is known, aluminum hydroxide is an adsorbent with amphoteric properties. At relatively high pH values, mainly cations are adsorbed, and the adsorption of zinc and nickel increases with increasing pH (Fig. 4), reaching maximum values at a definite pH; in presence of a slight excess of ammonia it begins to decrease.

A number of workers found that the pH at which precipitation of metal salts begins depends on the salt concentration [16, 17]. For example, it was found for the system $\text{ZnSO}_4\text{--ZnO--H}_2\text{O}$ that precipitation of zinc begins at pH = 6.71 when its concentration is 0.0154 g-ion/liter, and at pH = 5.38 when C_{Zn} is 2.234 g-ions/liter. For the system $\text{NiSO}_4\text{--Ni}(\text{OH})_2\text{--H}_2\text{O}$ the precipitation of nickel in the form of hydroxide begins at pH = 8.12 when the concentration is 0.0014 g-ion/liter, and at pH = 6.65 when its concentration is 1.343 g-ion/liter [17]. The same authors found that the pH values which must be reached for precipitation of metal salts as hydroxides vary in parallel to their solubility products [17].

Apparently because of this the adsorption of metal ions on amorphous precipitates, including aluminum hydroxide, greatly depends on the pH of the medium and on the concentration of the adsorbate. Moreover, the adsorption also depends on the isoelectric state of the $\text{Al}(\text{OH})_3$ ampholyte. In presence of excess ammonia, despite the high pH, the adsorption of nickel and zinc ions by aluminum hydroxide falls fairly sharply owing to formation of complex zinc and nickel ammine ions, which are adsorbed and coprecipitated to a considerably smaller extent than the simple ions.

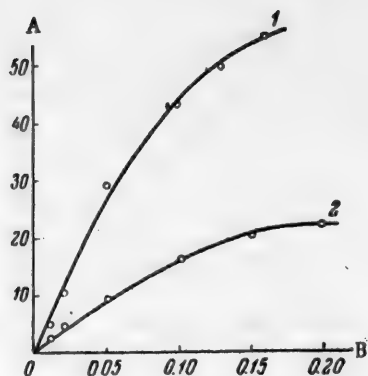


Fig. 3. Effect of aluminum salt concentration on adsorption of nickel and zinc by aluminum hydroxide; zinc and nickel salt concentrations constant at 5 millimoles/liter. A) Amount of bivalent metal adsorbed (%), B) $\text{Al}_2(\text{SO}_4)_3$ concentration (N). Adsorption isotherms for: 1) zinc, 2) nickel.



Further increase of the ammonium hydroxide concentration suppresses the degree of dissociation of the complex zinc and nickel amines increasingly with additional NH_4OH concentration, with a consequent decrease of the adsorption of nickel and zinc (Table 2). The precipitation was carried out in presence of 1.12 molar NH_4Cl at 60° and $\text{pH} = 10.6$.

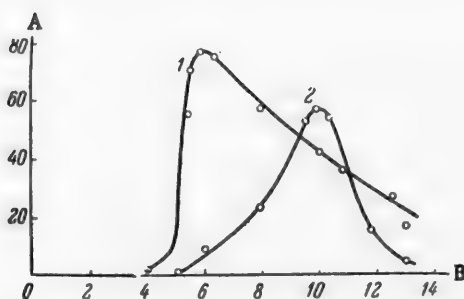


Fig. 4. Effect of solution pH on the adsorption of nickel and zinc by aluminum hydroxide. NH_4Cl concentration 0.37 mole/liter. A) Amount of metal adsorbed (%), B) solution pH. Adsorption curves for: 1) zinc, 2) nickel.

Precipitation of aluminum as the hydroxide ceases at $\text{pH} \sim 5$ [18, 19] at the aluminum concentrations studied. At $\text{pH} > 8$ a small part of the hydroxide dissolves, forming ammonium aluminate. However, although at high pH values only a very small amount of aluminum hydroxide dissolves, zinc and nickel are coprecipitated in larger amounts under those conditions than at $\text{pH} = 4-5$. Therefore the best medium for precipitation of $\text{Al}(\text{OH})_3$ is an ammoniacal medium of $\text{pH} = 5$ for separation of nickel, and a medium of $\text{pH} = 4$ for separation of zinc.

It follows from Table 2 that excess ammonia, by creating the conditions for formation of stable zinc and nickel complex amines, decreases the adsorption of these metals by aluminum hydroxide. Maximum adsorption of nickel and zinc occurs at low ammonia concentrations. Decrease of the adsorption of these ions corresponds to increased adsorption of ammonium ions, which decreases the degree of coprecipitation of nickel and zinc; with increasing concentration of ammonia the solubility of the hydroxides of these metals increases, and this also has a very strong influence on the nature of the adsorption. By the reaction of zinc and nickel hydroxides with ammonia, new complex bases are formed, which are stronger bases than NH_4OH and increase the pH of the solution.

For studies of the influence of NH_4Cl concentration on the adsorption of zinc and nickel, a mixture consisting of 0.1 molar aluminum sulfate solution and $5 \cdot 10^{-3}$ moles/liter of nickel and zinc sulfates was taken. The precipitation was performed with 25 ml of concentrated (20%) ammonia in presence of various concentrations of NH_4Cl ; the pH was 10.6; the total volume of the mixture was 100 ml. The results of the experiments are given in Table 3.

It follows from Table 3 that the coprecipitation of nickel and zinc is sharply diminished in presence of a large amount of ammonium salt. As stated earlier, in this case the substituting action of the ammonium ions is so great that it has a considerable influence on the adsorption of nickel and zinc cations. The coprecipitation of Ni^{++} and Zn^{++} ions by a mixture of ammonia with excess of ammonium salts is diminished to an even greater extent. Addition of ammonium salts prevents coprecipitation of copper to a considerable extent, owing to the suppression of the adsorption of copper by ammonium ions. Thus, a solution containing

a relatively small excess of ammonia and a large amount of ammonium salts has a very favorable effect in preventing the coprecipitation of nickel and zinc by ammonium hydroxide; in many cases the coprecipitation of these ions can be reduced to extremely low values, although it cannot be completely avoided.

Finally, we studied the influence of the concentration of nickel and zinc sulfates on their adsorption by aluminum hydroxide in presence of 1.12 mole/liter of ammonium chloride in the precipitation of 0.1 molar aluminum sulfate by 35 ml of 20% ammonia solution. The precipitate was shaken for 60 minutes, filtered, dissolved in 2 N sulfuric acid solution, and analyzed polarographically.

TABLE 2

Effect of NH_4OH Concentration on the Adsorption of Nickel and Zinc Ions (Concentration of aluminum solution 0.1 mole/liter, initial concentrations of nickel and zinc $5 \cdot 10^{-3}$ mole/liter, NH_4Cl concentration 1.12 mole/liter, $t = 60^\circ$, $\text{pH} = 10.6$)

NH_4OH concentration (moles/liter)	Adsorption of			
	nickel		zinc	
	in mg/100 ml	in %	in mg/100 ml	in %
0.2	11.0	37.7	22.1	67.5
0.8	2.4	8.2	7.3	22.4
1.6	1.78	6.1	4.45	13.6
3.2	0.952	3.25	—	—
6.4	0.536	1.83	1.46	4.5

TABLE 3

Effect of NH_4Cl Concentration on the Adsorption of Nickel and Zinc by Aluminum Hydroxide (NH_4OH concentration 2.95 moles/liter, $t = 60^\circ$, $\text{pH} = 10.6$)

NH_4Cl concentration (moles/liter)	Adsorption of			
	nickel		zinc	
	in mg/100 ml	in %	in mg/100 ml	in %
0.370	1.41	4.80	5.61	17.0
0.745	1.13	3.84	3.63	12.4
1.12	—	—	3.04	10.4
1.494	0.987	3.4	—	—
1.870	0.900	3.1	2.57	8.7

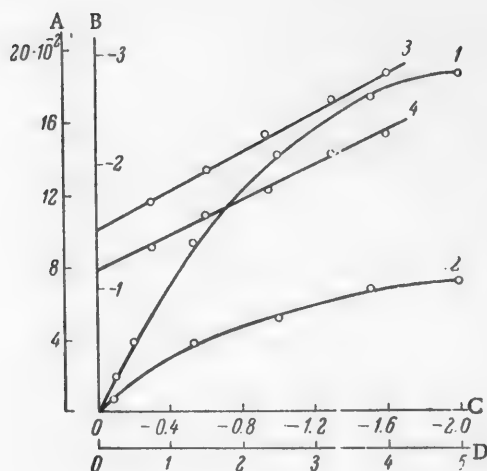


Fig. 5. Effect of concentration of nickel and zinc on their adsorption by aluminum hydroxide. A) Amount of metal adsorbed x/m (in mg-ions), B) $\log x/m$, C) $\log C$, D) MeSO_4 concentration (in millimoles/liter). Adsorption isotherms of: 1) zinc, 2) nickel. Logarithmic adsorption plots of: 3) nickel, $1/n = 0.78$, $\log a = -1.5$, 4) zinc, $1/n = 0.68$, $\log a = -1.2$.

The adsorption isotherms of nickel and zinc ions, based on the analytical data, are plotted in Fig. 5. It is seen that the adsorption increases with concentrations of the adsorbed nickel and zinc ions. However, the ratio of the amount absorbed to the total amount present in the liquid phase decreases. In our experiments the relative adsorption of nickel decreased from 9.0 to 3.7%, and that of zinc from 20 to 9.0%. The experimental data on the adsorption of nickel and zinc ions in relation to their concentrations in solution are in good agreement with the Freundlich isotherm (Fig. 5, Curves 1 and 2):

$$\frac{x}{m} = ac^{\frac{1}{n}},$$

where $\frac{x}{m}$ are the amounts of nickel and zinc ions adsorbed, in mg-ions per 1 g of adsorbent, a and $\frac{1}{n}$

are empirical constants, and c is the equilibrium concentration of the salts of the ions, in millimoles/liter.

The constants a and $\frac{1}{n}$ were calculated from the

experimental data (Lines 3 and 4, Fig. 5):

$$a_{\text{Ni}} = 0.0316, a_{\text{Zn}} = 0.063, \frac{1}{n_{\text{Ni}}} = 0.78, \frac{1}{n_{\text{Zn}}} = 0.68.$$

SUMMARY

1. It is shown that with increasing concentration of ammonium hydroxide, up to a certain limit, the coprecipitation of nickel and zinc falls to negligible values, while aluminum hydroxide dissolves to only a small extent.

2. It is shown that by increase of the NH_4Cl concentration, the NH_4OH concentration can be reduced to a level at which $\text{Al}(\text{OH})_3$ is almost insoluble, while the coprecipitation of nickel and zinc remains negligible owing to exchange adsorption of NH_4^+ ions with displacement of Ni^{++} and Zn^{++} ions.

3. The adsorption of nickel and zinc ions by aluminum hydroxide conforms to the empirical Freundlich equation.

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THE ELECTRODEPOSITION OF MANGANESE

I. V. Ianitskii and B. B. Stul'pinas

The Kaunas Polytechnic Institute

The electrodeposition of manganese has certain peculiarities which stem from the position of manganese in the potential series, and some very diverse factors influence the properties of the metal deposited on the cathode. Since the standard potential of the system Mn/Mn^{++} is even more negative than the corresponding potential for zinc, and reaches -1.18 v [1], the cathodic deposition of manganese is inevitably accompanied by liberation of considerable amounts of hydrogen, and it is possible at all only owing to the high overvoltage of hydrogen on manganese. Therefore the current efficiency in the electrodeposition of manganese is not high, and generally does not exceed 50-60% [2, 3].

Among the other factors which hinder the formation of satisfactory deposits of manganese, mention should be made, first, of the anodic oxidation of Mn^{++} ions, leading to the formation of a suspension of manganese dioxide; some consider that to avoid this the anolyte and catholyte should be separated by a diaphragm [4]; second, the formation of black, "burnt" deposits — a very common effect, which may be caused by contamination of the electrolyte, or deviations from the necessary conditions of electrolysis.

This communication contains the results of experiments which led to the formation of good — smooth and compact — manganese deposits in simple electrolysis conditions, with considerably improved current efficiency.

EXPERIMENTAL METHODS

The electrolytes were solutions containing 100 or 200 g/liter of $MnSO \cdot 5H$ and 75 g/liter of $(NH_4)_2SO_4$ (100/75 Electrolytes respectively). In experiments with a single anode, with deposition of manganese on one side of the cathode, the electrolyte volume was about 150 ml; in bilateral deposition, it was 250 ml. The electrolyte temperature was 18-25°. The electrolyte must be stirred at such a rate that any deposits of turbidity remain in suspension.

Square cathodes 4 or 10 cm² in area were cut from polished tin-plated copper or iron. The cathodes intended for single-sided coating were lacquered on one side. The cathodic-polarization curves were determined by the usual compensation method with small cathodes (4 cm²) lacquered on one side and fixed in a special plastic frame.

Our experiments were performed without the use of diaphragms, with lead-alloy anodes (97% Pb + 3% Ag or 97% Pb + 2% Ag + 1% As). To prevent the penetration of manganese dioxide, formed by anodic oxidation of Mn^{++} ions, into the electrolyte, the anodes were tightly wrapped in two or three layers of cotton fabric [3, 5, 6] and subjected to pretreatment which proved very important for normal operation.

The anodes were first subjected to anodic polarization in dilute sulfuric acid, and then in the usual manganese electrolyte. This removed extraneous metallic impurities from the anode surface. The wrapping is best done after partial treatment in the manganese electrolyte. As a result of the treatment the anodes become coated with a film of PbO_2 [7] and then with a firm layer of MnO_2 [3]. In experiments with well-prepared anodes the inner layer of the wrapping usually adheres to the anode after some tens of hours, by the action of the MnO_2 formed, while the outer layer becomes brownish only in parts. Therefore very little MnO_2 can penetrate into the electrolyte, provided that the anode current density does not exceed 5-6 amps/dm². At higher

current densities intense evolution of oxygen takes place with formation of finely divided MnO_2 , which has an adverse effect both on the quality of the manganese deposit and on the cathode current efficiency.

Anodes temporarily out of use should be stored in their wrappings, in water, to prevent destruction of the wrapping.

It is known [8-11] that a considerable hindrance in the formation of good-quality manganese deposits or coatings is contamination of the electrolyte by even very small amounts of impurities present in the original chemicals. We used manganese sulfate of the most readily available "pure" grade and concluded that the rather complicated methods recommended by some authors [8-10] for purification of the electrolyte are unnecessary. In most cases it is sufficient to prepare concentrated, almost saturated, solutions of MnSO_4 and $(\text{NH}_4)_2\text{SO}_4$ and to filter them, using the filtrates for making the electrolytes of required composition. In many cases the electrolyte quality is also improved if the pH is raised above 7 by addition of ammonia, followed by filtration to remove the precipitate formed.

We found that a very effective method of purifying the electrolyte is to add 1-3 g/liter of ammonium sulfate, to take the pH a little above 7 by addition of ammonia, and to filter off the hydroxide formed. The bulky precipitate very effectively adsorbs the impurities, including those present in the colloidal state, which decrease the current efficiency and lower the quality of the manganese deposit on the cathode. This method is essentially analogous to purification of the electrolyte with the use of iron hydroxide, recommended by some authors [8, 9, 11], but it has the advantage that it does not require oxidation of the electrolyte for conversion of ferrous into ferric iron.

We found that hydroxides of the elements of the titanium subgroup, especially zirconium hydroxide, produce the same effect.

The pH of the electrolyte was measured by means of the quinhydrone electrode. Curves for the titration of the electrolyte by ammonia and sulfuric acid (Fig. 1) show that the most favorable pH ranges, from the point of view of buffer action, are $\text{pH} = 2-3$ and $\text{pH} = 7-7.8$. At $\text{pH} > 7.8$, $\text{Mn}(\text{OH})_2$ starts to precipitate and is appreciably oxidized by atmospheric oxygen. Our experiments showed that in general it is preferable to carry out the electrolysis in the weakly alkaline medium indicated above. This gives smooth, bright or semidull coatings, and at low cathode current densities (up to 20 amps/dm²) the current efficiency increases with increase of pH. Moreover, under these conditions penetration of impurities into the manganese coating is less likely, as the hydroxides of many metals coagulate in this pH range.

As the electrolyte pH gradually decreases during the electrodeposition of manganese without the use of a diaphragm, it must be maintained constant by periodic additions of ammonia [5]. To maintain the pH constant we also introduced an auxiliary anode, enclosed in a microporous ceramic diaphragm, into the electrolyte. If only an anode in a diaphragm was used, this would, of course, raise the pH. In this case, by suitable adjustment of the current load on each anode, it is possible to maintain constant pH even during prolonged electrolysis.

Current efficiency and dendrite formation. If the anodes are properly pretreated and the electrolyte purified at intervals (see above), it is possible to obtain a reproducible current efficiency in the electrolysis. We determined the current efficiency in terms of total manganese deposited and also in terms of the weight of the compact, smooth deposit after removal of dendrites.

When manganese is deposited on one side of the cathode only, the current efficiency is 2-3% lower and more dendrites are formed than when both sides of the cathode are used. The results plotted in Fig. 2 were obtained in bilateral deposition on similar cathodes from electrolytes of pH 7.0-7.5, the quantity of electricity being the same in each experiment - 4 amp-hrs/dm². It is seen that dendrite formation is very considerable, and increases with increasing current density.

Comparison of Curves I and II shows that the current efficiency is decreased only slightly with decrease of the manganese sulfate concentration in the electrolyte from 200 to 100 g/liter of $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$. At high current densities dendrite formation decreases appreciably when the less concentrated electrolyte is used - the lower curves for the two electrolytes almost coincide.

The results of our experiments did not confirm the conclusion of Terekhov, Reikhshtadt, and Ivanova [5], who used electrolytes of the same composition, that the current efficiency passes through a maximum at current

density 25-30 amps/dm². In our experiments (Fig. 2) the current efficiency rose continuously up to very high current densities. However, if the additive discovered by us is used (see below), which greatly increases the current efficiency, the current efficiency passes through a maximum.

Improvement of current efficiency by addition of selenious acid. In the cathodic deposition of manganese, many workers add SO₂, or sulfite as recommended by Shelton [12], to the electrolyte; this gives compact deposits at lower current densities with somewhat higher current efficiencies [9, 13, 14]. Opinions differ on the manner of action of such additives.

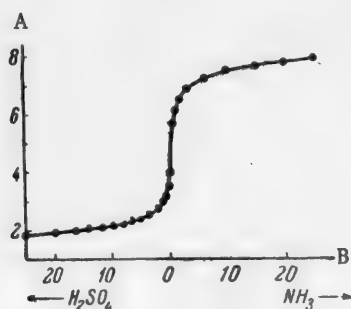


Fig. 1. Titration curve of Electrolyte 100/75 (1 liter). A) pH, B) amounts of 3 N H₂SO₄ and NH₃ solutions (in ml).

dal solutions. Therefore if the action of sulfurous acid or sulfite depends on the formation of colloidal sulfur at the cathode, a similar result should be obtained if they are replaced by selenious acid.

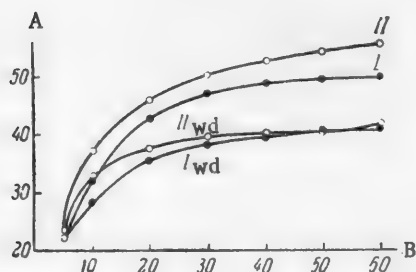


Fig. 2. Effect of current density on current efficiency. A) Current efficiency (%), B) current density (amps/dm²). Efficiencies: I) with dendrites from Electrolyte 100/75, I_{wd}) without dendrites from Electrolyte 100/75, II) with dendrites from Electrolyte 200/75, II_{wd}) without dendrites from Electrolyte 200/75.

the reproducibility of the yields leaves much to be desired. At the current densities used, the results were reproducible to within 1% if constant electrolysis conditions were maintained.

It follows from the graph (Fig. 3) that with addition of selenious acid good manganese coatings can be obtained with current efficiencies up to 90% and somewhat higher. An interesting feature is that a maximum current efficiency is found at relatively low current densities (2-5 amps/dm²). The coatings obtained under these conditions are microcrystalline, smooth, semidull, and pale, resembling the surface of aluminum articles in external appearance. Almost no dendrites appear in the 2-5 amps/dm² range.

Agladze [13] considers that the positive effect of sulfurous acid is the result of its reduction to elemental sulfur, which is in a finely divided state and forms a colloid which has a favorable influence on the electrolysis. According to Hammerquist [10], sulfurous acid acts by preventing oxidation of the purified solution. Shatalov and Isaev [4] also state that a reducing medium must be maintained in the cathode space; for this they add small portions of sodium sulfite to the electrolyte. Certain other authors [16, 17] cast doubt on the suitability of this additive.

These results suggested the use of selenious acid as an additive to the electrolyte. Selenious acid cannot create a reducing medium in the electrolyte, but is itself easily reduced. The elemental selenium formed in the reduction of selenious acid readily forms colloidal solutions.

Even the preliminary experiments showed that small amounts of selenious acid greatly increase the current efficiency. The best results are obtained with selenious acid concentrations of about 0.1-0.2 g/liter, which is close to the concentrations of sulfurous acid or sulfite recommended by the above authors. Even smaller amounts of selenious acid increase the current efficiency appreciably. If an excessive quantity of selenious acid is used, the colloidal selenium formed at the cathode first colors the electrolyte red rapidly, and then coagulates at the cathode and lowers the quality of the manganese deposit; this is usually associated with a fall of current efficiency. The optimum acidity of the electrolyte when selenious acid is added is pH = 7-7.5.

Figure 3 shows the variations of current efficiency with current density with additions of selenious acid (upper curves) and under the same conditions without the additive (lower curves). Only low current densities were used (up to 15 amps/dm²), as at higher densities

At current densities above 5 amps/dm² dendrite formation becomes appreciable at the cathode edges, and increases with the current density. At the same time the deposit darkens somewhat, and becomes more

lustrous from the edges of the cathode. Decrease of the current density to 0.5-1 amp/dm² also increases the luster, but under these conditions selenium tends to form a black sooty deposit on the cathode; however, this can be easily rubbed off.

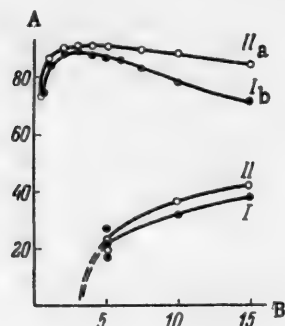


Fig. 3. Effect of addition of 0.1 g/liter of H_2SeO_3 in the current efficiency. A) Current efficiency (%); B) current density (amps/dm²). Efficiencies from Electrolyte 100/75; I) without additive; from Electrolyte 200/75; II) without additive, II_a) with additive.

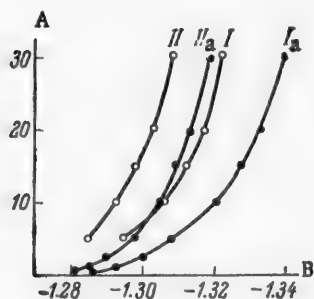


Fig. 4. Cathodic polarization curves. A) Current density (amps/dm²), B) cathode potential (v). Curves: I and I_a) Electrolyte 100/75 without and with added H_2SeO_3 , respectively; II and II_a) Electrolyte 200/75 without and with added H_2SeO_3 , respectively.

Manganese coatings obtained from electrolytes containing added selenious acid contain 0.2-0.5% of selenium, mainly in the form of $MnSe$; when the coatings are dissolved in acids, H_2Se and a little selenium is liberated. This small admixture of selenium increases the chemical resistance of the coatings; they dissolve more slowly in the electrolyte (without current) than coatings obtained without the use of selenious acid. Coatings containing selenium and treated with dichromate solution are also more resistant to atmospheric action.

The selenious acid added to the electrolyte is, of course, eventually consumed. To maintain its concentration in the conditions described, 5-10 mg/liter of H_2SeO_3 should be added after 1 amp/hour.

The reason for the great increase of current efficiency on addition of selenious acid is evidently the increase of the hydrogen overvoltage on manganese containing traces of selenium. The polarization curves in Fig. 4 show that the cathodic polarization is somewhat increased by this additive. A more detailed explanation of the mechanism of the action of selenious acid on the electrodeposition of manganese at present involves considerable difficulty.

SUMMARY

1. For successful electrodeposition of manganese without the use of diaphragms, preliminary treatment of the insoluble anodes is necessary.
2. With electrolytes without special additives, the current efficiency with respect to manganese increases with the current density up to very high current densities.
3. The current efficiency with respect to manganese is very much increased by addition of selenious acid; it passes through a maximum ($\sim 90\%$) at about 3-4 amps/dm².
4. The action of selenious acid is attributed to increase of the hydrogen overvoltage on manganese containing traces of selenium.

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GAS SATURATION IN THE ELECTROLYSIS OF WATER

A. L. Rotinian and V. M. Aloits

(Chair of Electrochemistry, the Leningrad Technological Institute, Leningrad)

Despite the great importance of gas saturation in the electrolysis of water, it has not been studied sufficiently.

The increase of the electrolyte resistance as the result of gas saturation is formally represented by the coefficient K in the formula for the potential drop in the solution:

$$e = KI_{\rho} \frac{l}{s}, \quad (1)$$

where I is the current strength, s is the cross-sectional area of the electrolyte, l is the distance between the electrodes, and ρ is the specific resistance of the electrolyte.

The coefficient of increased resistance may be expressed as the ratio of the resistances of the electrolyte with gas bubbles (R) and without (R_0):

$$K = \frac{R}{R_0}. \quad (2)$$

The coefficient of increased resistance and the gas saturation (Γ) are connected by the Rayleigh and Mashovets equations [1].

For nonconducting spherical inclusions and low values of gas saturation, the Rayleigh equation has the form:

$$K = \frac{1 + 0.5\Gamma}{1 - \Gamma} \approx \frac{1}{1 - 1.5\Gamma}. \quad (3)$$

The empirical equation of Mashovets, valid for any degree of gas saturation, may be written:

$$K = \frac{1}{1 - 1.78\Gamma + \Gamma^2}. \quad (4)$$

It follows from these equations that the coefficient of increased resistance of the electrolyte depends only on the gas saturation. Therefore the value of K at equal gas saturations should not depend on any technological factors.

To the best of our knowledge, no adequate experimental data in confirmation of the above are available in the literature [2, 3]. Therefore the first task in the present investigation was to study the increase of electrolyte resistance as a function of gas saturation, with different cathode materials, electrolyte compositions, and temperatures.

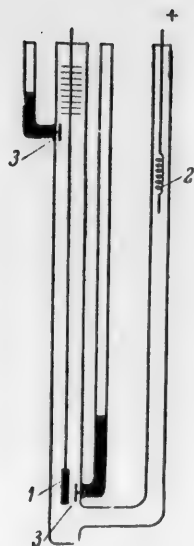


Fig. 1. Vessel for measurement of gas saturation and the coefficient of increased resistance. 1) Cathode, 2) anode, 3) platinized platinum plates for measurement of the electrolyte resistance.

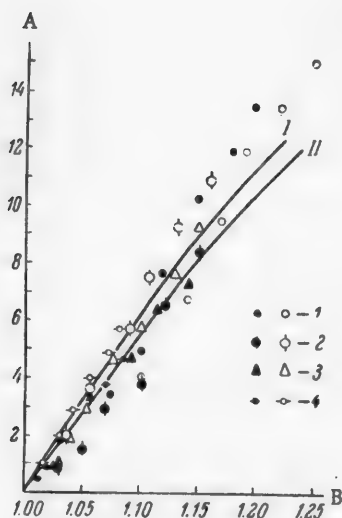


Fig. 2. Variation of gas saturation with the coefficient of increased resistance. A) Gas saturation (%), B) coefficient K. Cathode materials: 1) cadmium, 2) nickel, 3) iron and platinum, 4) cobalt. Curves corresponding to I) Rayleigh equation, II) Mashovets equation.

The apparatus shown in Fig. 1 was used for determinations of the coefficient of increased resistance and of the gas saturation. The scale at the top of the vessel gave the increase of the electrolyte level as the result of electrolyte saturation with gas bubbles. Two platinum electrodes 22 cm apart were sealed into the vessel, for the resistance measurements. The inner diameter of the cathode space was 0.8 cm.

The gas saturation was found from the equation

$$\Gamma = \frac{\Delta h}{h + \Delta h} \cdot 100\% \quad (5)$$

where h is the height of the liquid column from the lower edge of the cathode to the meniscus, and Δh is the increase of liquid level as the result of gas saturation. The cathode area was 2 cm².

Variations of the coefficient of increased resistance with the gas saturation, for nickel, cobalt, iron, cadmium, and platinum cathodes at 20° are plotted in Fig. 2. The black points correspond to electrolysis of 25% KOH solution, and the others, to electrolysis of 17% NaOH solution.

The K- Γ relationships at 20 and 80° in the electrolysis of 17% NaOH solution with a nickel cathode are plotted in Fig. 3.

It follows from Figs. 2 and 3 that the coefficient of increased resistance depends on the gas saturation only. For a given gas saturation, the coefficient of increased resistance does not depend on the cathode material, electrolyte composition, or the temperature, in the ranges studied.

In Fig. 2, Curve I was calculated from the Rayleigh equation, and Curve II from the Mashovets equation.

At low gas saturations, both equations give almost equally satisfactory agreement with the experimental data.

The effects of current strength (density) and temperature on the gas saturation were next studied. The results of the experiments are plotted in Figs. 4 and 5. It follows from Fig. 4 that the gas saturation increases linearly with the current passing through the electrode, and greatly depends on the electrolyte material. The gas saturation was greatest in electrolysis with cadmium cathodes and least in electrolysis with platinum cathodes.

Figure 5 shows that, under equal conditions, gas saturation decreases with rise of temperature.

Gas saturation must evidently be less if the hydrogen bubbles are removed more rapidly from the electrolyte.

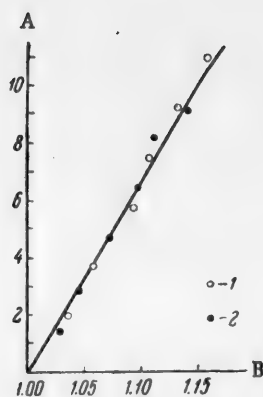


Fig. 3. Effect of gas saturation on the coefficient of increased resistance at 20° (1) and 80° (2). Nickel cathode. A) Gas saturation (%), B) coefficient K.

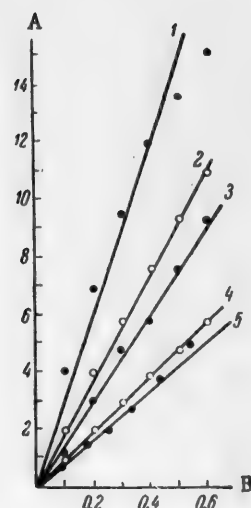


Fig. 4. Effect of current strength and electrode material on gas saturation. Electrolyte 17% NaOH solution, $t = 20^\circ$. A) Gas saturation (%), B) current strength (amp). Cathode materials: 1) cadmium, 2) nickel, 3) iron, 4) cobalt, 5) platinum.

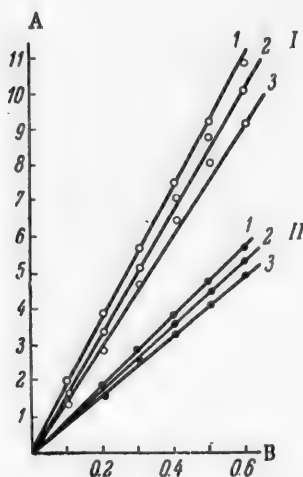


Fig. 5. Effect of temperature on gas saturation. A) Gas saturation (%), B) current strength (amp). Temperature ($^\circ\text{C}$): 1) 20, 2) 40, 3) 80. I) Nickel, II) cobalt.

By Stokes' law, the velocity of ascent of the bubbles is proportional to the square of their radius or to the volume to the power $2/3$.

Gas saturation must therefore be inversely proportional to the bubble volume to the power $2/3$. According to Frumkin and Kabanov [4], the volume of the gas bubbles detaching from the electrode surface is determined by the action of electrocapillary and gravitational forces. They considered the detachment of a bubble from a horizontal surface. The detachment of a bubble from a vertical cathode surface was analyzed by Piontelli [5].

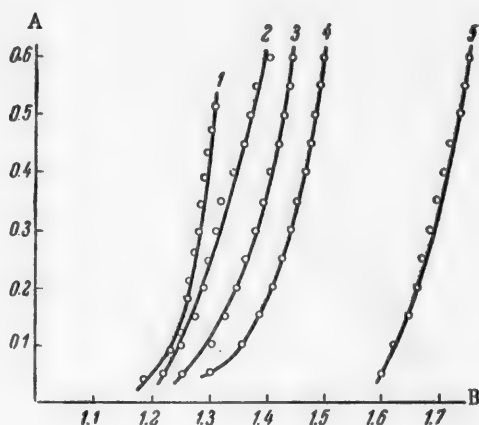


Fig. 6. Cathodic polarization curves in 17% NaOH solution at 20° . A) Current strength (amp), B) negative cathode potential (v). Cathode materials: 1) platinum, 2) cobalt, 3) iron, 4) nickel, 5) cadmium.

Since the interfacial tension at the metal-electrolyte boundary depends on the electrode potential, the bubble volume, according to Frumkin and Kabanov, must also depend on the electrode/electrolyte interfacial tension, decreasing as the potential moves further away from the point of zero charge of the electrode. Consequently, the different values for the gas saturation found with the use of different metals for the cathodes must be determined by the difference between the potential of the operating cathode and the zero-charge potential.

The second task in our investigation was to verify this.

The polarization curves for cadmium, nickel, cobalt, iron, and platinum cathodes in 17% NaOH solution at 20° were determined by the usual compensation method. The results are plotted in Fig. 6. The differences between the cathode potentials at $I = 0.5$ amp and the zero-charge potentials of the metals were then found. The results were correlated with the values of the gas saturation (see Table).

Variation of Gas Saturation with the Difference Between the Cathode Potential and the Zero-Charge Potential

Cathode material	Cathode potential (in v) at $I = 0.5$ amp	Zero-charge potential (in v)	$\varphi_c - \varphi_{\text{zero}}$ charge (in v)	Gas saturation (%) at $I = 0.5$ amp
Cobalt . . .	-1.37	-0.50	-0.87	4.9
Platinum . . .	-1.31	-0.34	-0.97	4.5
Iron . . .	-1.43	-0.46	-0.96	7.6
Nickel . . .	-1.48	-0.38	-1.10	9.3
Cadmium . . .	-1.73	-0.68	-1.05	15.0

The zero-charge potentials were taken from the paper by Kheifets and Krasikov [6].

It must be pointed out that correlation of the gas saturations with the zero-charge potentials cannot give accurate results, as the zero-charge potentials in strongly alkaline media are not known for any of the metals used, and we had to extrapolate the graphical results given in Kheifets and Krasikov's paper.

Nevertheless, it may be claimed that our results qualitatively confirm the relationship between gas saturation and the difference between the cathode potential and zero-charge potential of its surface. Quite analogous results were obtained at 80°.

SUMMARY

1. The influence of various factors on gas saturation of the cathode space during electrolysis of water was studied, and it was shown that the coefficient of increased resistance depends only on the gas saturation. The coefficient of increased resistance, for a given gas saturation, does not depend on the cathode material, the electrolyte composition, or the temperature. At low gas saturations the relationship between K and Γ is described equally satisfactorily by the Rayleigh and by the Mashovets equations.
2. In the experimental conditions used, gas saturation increases linearly with current strength (density), decreases with increase of temperature, and depends on the cathode material.
3. It is shown that gas saturation increases with increase of the difference between the cathode potential and the zero-charge potential of its surface.

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ELECTROCHEMICAL OXIDATION OF CHROMIUM SULFATE

B. I. Tomilov

Scientific Research Institute of Organic Intermediates and Dyes

(Rubezhnoe Branch)

Among the various oxidizing agents used in the aniline dye industry, compounds of sexivalent chromium, mainly dichromates, are extensively used. After oxidation and isolation of the organic material, acid filtrates containing chromium sulfate are obtained. The lime treatment used at present cannot be regarded as at all a satisfactory process of filtrate treatment, as the valuable chromium is all wasted, in addition to the loss of sulfuric acid. Electrochemical regeneration of dichromate [1] is therefore of considerable interest. The regenerated mixture of sulfuric and dichromic acids can again be used for oxidation; this completes a cycle of indirect electrochemical oxidation.

The electrochemical oxidation of chromium sulfate was suggested by Fitzgerald [2]. In later years more detailed studies of the electrochemical oxidation of trivalent chromium were carried out [3], and different technical variations of the process were protected by a number of patents [4]. In most cases it was recommended to carry out the electrochemical oxidation in diaphragm cells. There are reports of the regeneration of chromic acid from liquors on the industrial scale. McKee [5] developed a laboratory method for continuous electrochemical oxidation of chromium sulfate. N. S. Drozdov [6] studied the electrochemical oxidation of chrome alum at relatively low concentrations.

It should be noted that in these investigations the electrochemical oxidation of trivalent chromium was studied in dilute solutions, with low contents of chromium sulfate and sulfuric acid. However, the greatest practical interest attaches to the possibility of regenerating solutions with high concentrations of chromium and sulfuric acid.

This paper contains the results of an experimental study of the electrochemical oxidation of trivalent chromium in concentrated solutions of sodium chromium sulfate containing sulfuric acid.

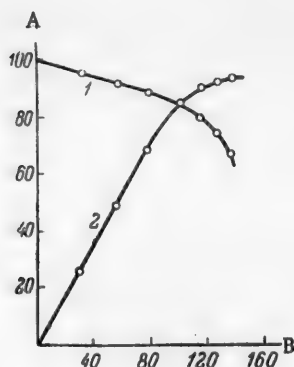
EXPERIMENTAL METHODS

Solutions of sodium chromium sulfate prepared by reduction of sodium dichromate with formaldehyde were used for the experiments.

Two types of cell were used. The cell of the first type was a glass beaker 1 liter in capacity, closed by a rubber bung. The anode was a lead cylinder which just fitted into the beaker. According to the required current density, the cathode was either a lead cylinder 12 mm in diameter, placed in the center of the beaker, or lead rods 6 and 3 mm² in cross section. No diaphragm was used in the electrolysis. The electrolyte volume was 900 ml.

The cell of the second type was a lead vessel, 3.5 liters in capacity, which acted as the anode. The cathode was a perforated lead cylinder inserted inside the diaphragm. The diaphragm was a porous fireclay beaker, internal diameter 80 mm, height 235 mm. The diaphragm was closed by a rubber bung and inserted on a rubber ring into the anode vessel. The bung had holes for a thermometer and the lead. The cathode and anode spaces of the cell were connected to reflux condensers by means of branch tubes. The catholyte

was 40% sulfuric acid, its volume being 550 ml. The anolyte, 1850 ml in volume, was the solution of chromium sulfate in sulfuric acid to be oxidized. The direct current was supplied from selenium rectifiers type VSA-6M.



Effect of quantity of electricity passed on the electrochemical oxidation of chromium sulfate. A) Yield (%), B) quantity of electricity passed (% of theoretical). 1) Current efficiency, 2) yield of chromic acid.

The current efficiency decreases with increase of current density from 3 to 5 amps/dm². The effectiveness of the electrochemical oxidation also decreases somewhat with increase of temperature from 55 to 80°.

The course of the electrochemical oxidation is shown in the Figure. The current efficiency and yield increase linearly with the quantity of electricity passed, up to a certain limit. Beyond this the current efficiency decreases sharply.

TABLE 1

Effect of Chromium Sulfate Concentration on the Current Efficiency (anolyte temperature 55°, $D_a = 3$ amps/dm², $D_k = 10$ amps/dm², quantity of electricity passed $Q = Q_{theoret.}$, average electrode voltage 3.7-4.7 v)

Anolyte composition (g/liter)		Anolyte composition after electrolysis (g/liter)		Current efficiency (%)	Loss in electrolysis (%)
Cr ⁺⁺	H ₂ SO ₄	total chromium content	total acidity		
46.0	55.0	44.8	39.2	250	85.3
75.0	55.0	74.2	66.8	375	89.2
77.5	55.0	76.2	70.7	390	91.2
99.0	55.0	95.4	85.4	470	86.3
113.5	55.0	110.3	92.0	490	81.0
169.5	55.0	156.0	120.0	585	71.3

Before the start of electrolysis the cathode and anode were treated in nitric acid until bright, and then washed thoroughly in water. The cell was placed in a bath with running water to keep it at the required temperature. The current strength was regulated by means of rheostats.

Electrochemical oxidation of trivalent chromium in a diaphragm cell. The results of the experiments are given in Tables 1-3 and in the Figure.

It follows from the data in Table 1 that the current efficiency depends on the concentration of the chromium salt in the original solution. The best yields are obtained at a certain optimum concentration, about 80 g/liter.

The effect of H₂SO₄ concentration on the current efficiency is given in Table 2. It is seen that the current efficiency decreases with increase of H₂SO₄ concentration. At a certain limiting concentration, about 800 g/liter H₂SO₄, the oxidation almost ceases.

The data in Table 3 show the variations of current efficiency with the electrolysis temperature and current

TABLE 2

Effect of H₂SO₄ Concentration on the Current Efficiency anolyte temperature 55°, $D_a = 3$ amps/dm², $D_k = 10$ amps/dm², quantity of electricity passed $Q = Q_{theoret.}$, average electrode voltage 3.7-5.3 v)

Anolyte composition (g/liter)		Anolyte composition after electrolysis (g/liter)		Current efficiency (%)	Loss in electrolysis (%)
Cr ⁺⁺	H ₂ SO ₄	total chromium content	total acidity		
75.0	55.0	74.2	66.8	375	89.2
75.0	275.0	73.5	61.8	580	82.5
70.0	375.0	68.0	55.3	625	79.0
70.0	575.0	67.3	47.0	800	67.2
70.0	850.0	57.4	11.7	800	17.8

TABLE 3

Effects of Current Density and Electrolysis Temperature on the Electrochemical Oxidation of Chromium Sulfate (quantity of electricity passed $Q = Q_{\text{theoret.}}$)

Anolyte composition (g/liter)		D_a (amps/dm ²)	D_k (amps/dm ²)	Temperature (°C)	Anolyte composition after electrolysis (g/liter)			Current efficiency (%)	Loss in electrolysis (%)
Cr ³⁺	H ₂ SO ₄				total chromium content	Cr ³⁺	total acidity		
75.0	45.0	3.0	7.0	80	73.6	65.7	384	87.5	1.9
77.5	55.0	3.0	7.0	55	76.2	70.7	390	91.2	1.7
77.5	80.0	5.0	11.6	55	74.9	62.2	394	80.2	3.3

Electrochemical oxidation of trivalent chromium in a cell without a diaphragm. The diaphragm is one of the most vulnerable parts of an electrolytic cell. It was therefore important to study the possibility of oxidation of Cr³⁺ in a cell without a diaphragm. Special measures, one of which is increase of the cathode current density, must be taken to prevent reduction of chromic acid at the cathode.

The results of the experiments are given in Table 4.

TABLE 4

Effect of Sulfuric Acid Concentration on the Degree of Electrochemical Oxidation of Trivalent Chromium in a Cell without a Diaphragm (Average electrolysis temperature 70°, $D_a = 4.5$ amps/dm², quantity of electricity passed $Q = Q_{\text{theoret.}}$)

Electrolyte composition		D_k (amps/dm ²)	average electrode voltage (v)	Comp. of electrolyte at end of exp. (g/liter)			Current efficiency	Loss in electrolysis (%)
Cr ³⁺	H ₂ SO ₄			total chromium content	Cr ³⁺	total acidity		
80.0	65.0	25	4.2	79.5	2.0	70.0	1.5	0.6
80.0	65.0	125	6.8	79.0	2.0	70.0	1.5	1.2
80.0	250.0	25	3.0	78.5	14.2	225.0	17.7	1.9
80.0	250.0	125	7.0	78.0	19.4	240.0	24.2	2.5
80.0	350.0	25	3.0	78.8	22.8	451.0	28.5	1.5
80.0	350.0	125	5.3	78.0	26.4	476.0	33.0	2.5
75.0	390.0	25	3.0	73.0	30.4	476.0	40.6	2.7
75.0	390.0	125	4.0	73.2	33.9	498.0	45.2	2.4
80.0	450.0	25	3.0	78.0	44.6	597.0	55.7	2.5
80.0	450.0	125	4.7	78.0	56.0	647.0	70.0	2.5
80.0	650.0	25	3.6	77.6	19.5	745.0	24.4	3.0
80.0	650.0	125	5.6	75.0	22.4	745.0	28.0	6.3
80.0	850.0	25	3.5	76.0	0.0	825.0	0.0	5.0
80.0	850.0	125	7.0	70.0	0.0	825.0	0.0	12.5

Examination of the data in Table 4 reveals a number of peculiarities in the electrochemical oxidation of Cr³⁺ in absence of a diaphragm. Oxidation proceeds with good yields only in a narrow range of acidity of the original solution. As the sulfuric acid concentration of the original solution increases, the current efficiency rises to a maximum at 450-500 g/liter H₂SO₄, and then falls sharply. It follows from the data in Table 4 that lower current densities correspond to lower current efficiencies.

DISCUSSION OF RESULTS

These results convincingly demonstrate the practical possibility and advisability of the electrochemical oxidation of Cr³⁺ at high concentrations of chromium sulfate and sulfuric acid in the original solution.

The observed decrease in the effectiveness of the electrochemical oxidation on increase of the Cr³⁺ concentration above the optimum value is probably due to an increase of the solution viscosity, which hinders

the diffusion of Cr^{3+} ions to the anode. In such cases the yield can be increased by agitation of the anolyte by means of compressed air.

The influence of H_2SO_4 concentration on the electrochemical oxidation of Cr^{3+} can be attributed to the low solubility of the CrO_3 formed on the anode in concentrated H_2SO_4 . When a certain limiting concentration of H_2SO_4 is reached, the anode becomes coated with a film of chromium trioxide, strong foaming begins, and oxidation almost ceases.

The values of the current efficiency in the region of optimum sulfuric acid concentration in the electrochemical oxidation of Cr^{3+} in a cell without a diaphragm suggest that the process without the use of a diaphragm is suitable for the electrochemical oxidation of Cr^{3+} . However, it must be remembered that it then becomes necessary to separate the hydrogen and oxygen evolved during the electrolysis.

Attention must be drawn to the increase of the sulfuric acid concentration during the electrochemical oxidation of chromium sulfate, and to the loss in electrolysis. In oxidation in a diaphragm cell these two effects are largely determined by factors associated with the diffusion of ions across the porous partition and the transference of ions by the action of electric current.

The chromium content of the catholyte was determined after the end of each experiment. In experiments in which the current efficiency was not too low, this content was approximately equal to the decrease of the total chromium content of the anolyte, and was the main source of loss in electrolysis.

Our results lead to the conclusion that, despite the view commonly held in the literature cited, increase of the sulfuric acid concentration in the anode compartment by transference from the cathode compartment does not play any significant role. The overall equation for the electrochemical oxidation of chromium sulfate



can be used to calculate the amounts of sulfuric and chromic acids formed by the oxidation of a definite quantity of chromium sulfate. The quantities of the acids found, in terms of equivalent sulfuric acid, are compared in Table 5 with the values calculated from the above equation.

TABLE 5

Comparison of Experimental and Calculated Values of the Acidity of the Anolyte after Electrochemical Oxidation of Chromium Sulfate

Amount of $\text{H}_2\text{SO}_4 + \text{H}_2\text{CrO}_4$ (g/liter)	Experiment Nos.					
	1	2	3	4	5	6
Calculated	240	370	392	460	489	621
Found	250	375	390	470	490	585

It is seen that the experimental and calculated values are very close. This shows that increase of the H_2SO_4 concentration in the anolyte is caused only by the anodic oxidation of Cr^{3+} .

SUMMARY

1. It was shown in experiments on the electrochemical oxidation of trivalent chromium in concentrated solutions of sodium chromium sulfate that dichromate can be regenerated electrochemically from industrial acid filtrates containing chromium sulfate and sulfuric acid.

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EFFECT OF AIR CONCENTRATION ON THE CORROSION OF ALUMINUM BY CHLORINE AT HIGH TEMPERATURES

Kh. L. Tseitlin and V. A. Strunkin

The K. E. Voroshilov Institute of Organic Intermediates and Dyes

Air has a strong influence on the corrosion of aluminum by dry chlorine [1]. It was of interest to determine the role of the air concentration in this process.

The experimental procedure was the same as that described previously [1-3]. Chlorine from a cylinder and air from a compressor were dried separately in wash bottles containing sulfuric acid, mixed in a flask containing glass wool, and passed through a preheating tube into the quartz apparatus for corrosion tests. The duration of each experiment was 6 hours, except in cases when the tests had to be stopped earlier owing to clogging of the tubes with corrosion products. The aluminum contained (in %): Fe 0.27, Si 0.12.

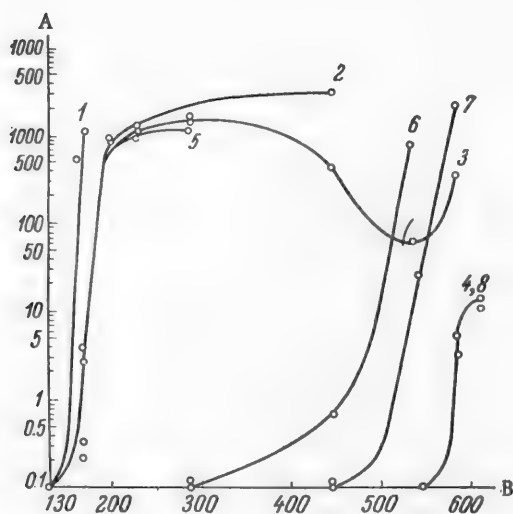
The results of the experiments are given in the Table and the Figure.

EXPERIMENTAL METHODS

Chlorine rate 420 ml/minute. Aluminum burns in chlorine at about 160° [3], but the temperature at which it catches fire is raised by the presence of even 0.2% of air. For example, at 170° the specimens remain bright and are attacked strongly only in the region of contact with the quartz hook. Above 190° aluminum burns in a current of chlorine containing 0.2% air.

The temperature at which the metal catches fire is higher in chlorine containing 4% air. For example, at 170° the specimens remain bright, and chlorination only begins after 2.5 hours; the region of contact with the quartz hook is considerably attacked. At about 230° the aluminum burns, while at 450-590° the rate of reaction decreases, especially at about 540°. Despite the strong corrosion of aluminum in a current of chlorine containing 4% air, the specimens did not melt and light was not emitted up to 590°.

Aluminum has good resistance up to 540° in a current of chlorine containing 17% air. At 590-616° the metal undergoes local attack, with formation of pits randomly distributed over the whole surface. No increase of temperature owing to heat of reaction was observed even at 616°.



Effect of air concentration on the corrosion of aluminum by chlorine. A) Corrosion (in $\text{g/m}^2 \cdot \text{hour}$), B) temperature ($^{\circ}\text{C}$). Chlorine and air rates respectively (in ml/minute): 1) 420 and 0; 2) 420 and 3; 3) 420 and 4; 4) 420 and 21; 5) 110 and 0; 6) 110 and 3; 7) 110 and 4; 8) 110 and 21.

Effect of Air Concentration on the Corrosion of Aluminum by Chlorine (in g/m²·hour) Duration of tests 6 hours

Rates (in ml/minute)		Corrosion (in g/m ² ·hour) at temperature (°C)										Notes
		130	160	170	200	230	290	450	540	590	616	
-	110	-	-	0.3	991.9*	955.5*	1029.0*	-	-	-	-	170° - specimen surface bright, considerable corrosion in zone of contact with quartz (pitting). 200° - aluminum catches fire after 1.5 hours; temperature in apparatus rises 20° per minute, reaching 420° at the end of the test. Specimens coated with a black sooty deposit after the tests; deposits insoluble in water, hydrochloric acid, or caustic solution Aluminum catches fire at 160°. Sharp rise of temperature 170-290° - specimens bright, pits formed up to 0.2 mm deep in some regions at 230-290°. 450° - local corrosion, surface covered with a white deposit containing chlorine. 540° - violent chlorination, sharp rise of temperature, fusion of specimens
	420	0.0	524.3**	1112.7**	-	-	-	-	-	-	-	
	3	110	-	0.0	-	0.1	0.1	0.7	833.8*	-	-	
3	420	0.0	-	26	834.2**	1424.0**	1560.0*	3126.0**	-	-	-	170° - specimens bright, considerable corrosion (pitting) in region of contact with quartz. 200° - aluminum catches fire, temperature rises 20-50° per minute, light emitted, specimens melt 450° - specimens bright, considerable corrosion in region of contact with quartz (pitting). 540° - no rise of temperature owing to heat of reaction. Specimens coated with a white film, insoluble in water. 550° - aluminum catches fire, temperature rises, causing melting of the specimens
	40	110	-	-	-	-	-	0.1	23.9	2168.0**	-	

* Duration of test 1.5-4 hours.

** Duration of test up to 60 minutes.

(continued)

Rates (in ml/minute Air chlo- rine		Corrosion (in g/m ² ·hour) at temperature (°C)										Notes
		130	160	170	200	230	290	450	540	590	616	
40	420	-	-	7.1 0.2 } 3.7	-	1244.0*	1525.0*	439.6*	62.8	347.4*	-	170° - specimens bright, considerable corrosion in region of contact with quartz. 230-290° - aluminum catches fire, temperature in apparatus rises 10° per minute. Dark gray corrosion products remaining on the specimens contain about 60% Al and 16% chlorine. At 450° the temperature rise reaches 7° per minute, and ceases completely at 540°. The specimens after the tests retained their rectangular shape, darkened somewhat at 450°, were coated with a gray deposit at 540°; at 590° a white deposit was formed. The corrosion products on the specimens contain chlorine; the powder does not effervesce in water and forms a considerable curdy precipitate with it
210	110	-	-	-	-	-	-	0.1	-	2.0	10.9	450° - specimens bright, with a few black pits. 590° - uniform corrosion, surface covered with a white film free from chlorine. 616° - pieces of snow-white film taken from the surface form an insoluble precipitate with water
210	420	-	-	0.2	-	-	0.1	0.1	0.1	5.0	13.0	Aluminum has good resistance up to 540°. Local attack above 580°. No temperature rise owing to heat of reaction observed

Chlorine rate 110 ml/minute. At considerable chlorine rates (250-420 ml/minute), aluminum burns rapidly at about 160°. The temperature at which aluminum catches fire is higher at 110 ml/minute. For example, at 170° the metal surface is almost unaffected by corrosion. A deep pit was found only in one specimen, in the region of contact with the quartz hook. Aluminum burns in chlorine at about 200°.

In a current of chlorine containing 1% air, the total rate of corrosion of aluminum at 170-290° is slight. The specimens remain bright, with pits in some regions. The general and local corrosion of aluminum increases as the temperature is increased to 450°. At 540° violent chlorination begins after 30 minutes.

Increase of the air concentration in chlorine to 13% greatly increases the chemical resistance of aluminum. The specimens remain bright even at 450°; a pit, resembling local burning of the material, is formed only at the point of contact with the quartz. At 590° a violent exothermic reaction begins as soon as the chlorine is admitted; this is accompanied by a sharp rise of temperature in the apparatus, and fusion of the specimens.

Aluminum is even more resistant in chlorine containing 44% air. Even at about 590° the total corrosion does not exceed 2 g/m²·hour; the specimens are uniformly covered with a white deposit free from chlorine.

When aluminum reacts with chlorine-air mixtures, aluminum oxide, oxychlorides and chloride may be formed in different proportions, according to conditions [4, 5].

Conditions which favor the formation of volatile aluminum chloride intensify destruction of the metal; if the conditions favor formation of oxide and oxychlorides, the corrosion rate decreases.

The reaction of formation of volatile aluminum chloride is increasingly retarded with increase of the air concentration in the chlorine, and, conversely, more nonvolatile corrosion products are formed on the aluminum surface. The length of the induction period, the corrosion rate, and the temperature at which the aluminum catches fire also depend on the concentration of air in the gas stream. As in cases studied previously [2], the chlorine rate is very significant.

When aluminum reacts with chlorine containing 4 % air, above 200° the volatile chloride (mainly) is formed, and a nonvolatile dark gray (up to 540°) or a white (at about 590°) deposit, insoluble in hot water, is formed on the metal surface. The deposit contains aluminum and chlorine, and probably consists of a mixture of oxychlorides and oxide of aluminum.

The appreciable decrease of corrosion of aluminum at about 500° may be attributed to the fact that under these conditions the rate of formation of aluminum chloride decreases, while the coating of nonvolatile corrosion products on the metal protects the surface more effectively against the corrosion action of chlorine.

In many cases the chlorination of different regions of the surface of industrial aluminum proceeds irregularly; this may be attributed to physicochemical heterogeneity and vulnerability of the film at points where impurities are present owing to decreased adherence of the film to the metal. However, it has been reported [4] that even particles of chemically pure microcrystalline aluminum oxide differ in activity; the most active particles quickly react with HCl at 1000°, or with chlorine at 1200°. The remaining, less active particles evidently react less vigorously with chlorine. The causes of this passivity are unknown.

The intensified corrosion of aluminum in the region of contact with the quartz hook may be explained as follows. Continuous access of oxygen to the metal surface is necessary to maintain the protective properties of the oxide film. However, when the oxygen concentration is low, its diffusion into the gap (slit) is greatly retarded, so that defects formed in the film are not covered over; this results in a violent reaction between chlorine and aluminum in the contact area where the protective coating is imperfect. The higher the chlorine concentration, the more oxygen is required to prevent slit corrosion. It should be noted in this connection that pitting corrosion in the gap does not occur in chlorine highly diluted with technical nitrogen (1:10) containing 0.5% oxygen. However, if the nitrogen is deoxygenated, the corrosion is intense. In discussing the mechanism of crevice corrosion, Rozenfel'd and Marshkov note [6] that, to maintain the passive state of iron in an electrolyte solution, continuous access of inhibitor is necessary; diffusion of inhibitor to the metal in the crevice is hindered, and its concentration may fall to a value at which passivity breaks down and corrosion pits are formed.

It is reported in the literature that film continuity is a most important condition for its ability to protect the metal against corrosion. Cracks and breaks in the films result in gas-permeable, vulnerable coatings [7]. We found, however, that any coatings, including porous or defective films, can retard attack of the material by chlorine at high temperatures. Aluminum burns in chlorine (passed at 420-250 ml/minute) at about 160°; a turbulent reaction begins after 30 minutes. If the specimens are put into bags made from glass filter cloth ("porous coatings"), a turbulent reaction begins only after 2 hours even at 200°. The probable explanation is hindered diffusion at the metal surface.

In a number of cases, nonvolatile gray or even black films are formed on the aluminum surface under the action of chlorine with air. It seems likely that these deposits consist of thin films of oxide and oxychloride, as in the blackening of aluminum in water [8].

Aluminum has high resistance in media in which a dense protective oxide film is formed rapidly on its surface. Because of its stronger oxidizing action, steam protects aluminum better than dry air. For example, when chlorine contains about 1% oxygen in the form of steam and air respectively, its corrosive effect on aluminum is shown by the following data:

Temperature (°C)	Corrosion (in g/m ² · hour)	
	Steam	Air
170	—	3.7
200	0.0	—
230	—	1244.0
290	0.3	1525.0
320	0.3	—
350	1667.0	—

The corrosion of aluminum in moist chlorine is slight even at 320°, whereas in a mixture of dry chlorine and air the metal already burns at 230°. When the concentrations of steam or air in chlorine are considerable, there are no appreciable differences in the corrosion rates of aluminum.

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THE SEARCH FOR STEELS RESISTANT TO LOW-NITROSE (DENITRATED) SULFURIC ACID

E. V. Zotova and A. A. Babakov

Denitrated sulfuric acid (76% H_2SO_4 and 0.05% HNO_3 , sp.gr. 1.675) leaves the tower at 120-135°, and is cooled down to 30-40° in an immersion cooler with lead coils through which water circulates.

The possibility of using acid-resisting steel instead of lead for heat-exchange equipment, including the cooler coils, has long attracted the attention of designers and sulfuric acid producers. However, because of the high corrosiveness of the medium, this problem presented considerable difficulties. The possibility of improving the technology of sulfuric acid production has only arisen with the development of new acid-resisting steels.

Chrome-nickel-molybdenum-copper alloy steels Cr18-Ni28-Mo3-Cu3* (EI-530), Cr23-Ni23-Mo3-Cu3 (EI-533), and Cr23-Ni28-Mo3-Cu3 (EI-629) [1], developed in recent years, are resistant to the action of sulfuric acid and have not yet been used widely enough.

Works trials of Cr18-Ni28-Mo3-Cu3 and Cr23-Ni23-Mo3-Cu3 steels in experimental welded coolers in the sulfuric acid of the Voskresensk Chemical Combine showed that both steels have good resistance to corrosion provided that the temperature of the cooler walls does not exceed 80°.

During the tests of the coolers made from these steels, considerable general and intercrystalline corrosion (especially of Cr18-Ni28-Mo3-Cu3) was observed at the welds of the side tubes (near the seams, the zone of the thermal influence) at the entry of the acid into the cooler, where the acid temperature reaches 120°. The cooler made from Cr18-Ni28-Mo3-Cu3 (EI-530) steel remained in service 2784 hours, and the cooler from Cr23-Ni23-Mo3-Cu3 steel, 10272 hours.

As these steels differ only by their chromium and nickel contents, it was of considerable practical and theoretical interest to study the influence of chromium and nickel on the corrosion of chromium-nickel-molybdenum-copper steels in low-nitrose (denitrated) sulfuric acid (76% H_2SO_4 and 0.05% HNO_3).

In connection with the proposal to make experimental spray coolers out of cast tubes, it was desirable to study the effects of chromium and nickel on the corrosion of cast steels in actual production conditions of the sulfuric acid unit of the Voskresensk Chemical Combine.

Low-carbon chromium-nickel-molybdenum-copper steels with different contents of chromium (5-27%) and nickel (9-28%), but with constant contents of molybdenum (3%) and copper (3%) were studied. The chemical composition of the experimental steels is given in Table 1.

Cylindrical specimens (25 mm in diameter and 55 mm high) were made from a cast bar previously quenched in water from 1200°. The specimens, suspended from wire made of Cr23-Ni28-Mo3-Cu3 steel, were placed in a conduit through which sulfuric acid flowed from the tower into the cooler at 35 m³/hour, at 120-135°. The specimens were tested continuously for 300 hours.

The results of the corrosion tests on the steels under production conditions are given in Table 2.

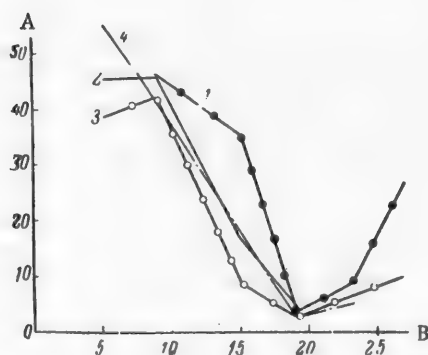
It follows from the data in this table that the corrosion rates of chromium-nickel-molybdenum-copper steels in denitrated sulfuric acid (76% H_2SO_4 and 0.05% HNO_3) vary at 130°, and depend more on the chromium than on the nickel content of the steel. The corrosion rate decreases more than 10-fold with increase of the *The symbols represent the elements present in the steel (Cr - chromium, Ni - nickel, Mo - molybdenum, Cu - copper), and the numbers following the symbols denote their % contents.

TABLE 1

Chemical Composition of the Tested Steels

Group	Steel grade	Contents of elements (%)				
		Cr	Ni	Mo	Cu	C
I	Cr5-Ni19-Mo3-Cu3	5.00	19.07	3.05	3.04	0.030
	Cr5-Ni23-Mo3-Cu3	4.90	23.15	3.05	3.14	0.025
	Cr5-Ni28-Mo3-Cu3	5.00	27.95	3.10	3.15	0.020
II	Cr9-Ni9-Mo3-Cu3	8.50	9.40	3.05	3.30	0.025
	Cr9-Ni15-Mo3-Cu3	8.80	14.5	3.05	3.00	0.030
	Cr9-Ni19-Mo3-Cu3	9.00	19.07	3.10	3.02	0.035
	Cr9-Ni23-Mo3-Cu3	9.00	23.50	3.05	3.24	0.030
	Cr9-Ni28-Mo3-Cu3	9.00	27.95	3.10	3.00	0.020
III	Cr15-Ni9-Mo3-Cu3	15.00	9.43	3.05	3.08	0.032
	Cr15-Ni15-Mo3-Cu3	14.50	14.95	3.10	3.00	0.035
	Cr15-Ni19-Mo3-Cu3	14.95	19.07	3.05	2.98	0.035
	Cr15-Ni23-Mo3-Cu3	15.00	22.93	3.02	2.97	0.035
IV	Cr19-Ni9-Mo3-Cu3	19.00	9.15	3.05	2.98	0.045
	Cr19-Ni15-Mo3-Cu3	19.00	14.87	3.07	3.00	0.045
	Cr19-Ni19-Mo3-Cu3	19.20	19.02	3.02	3.00	0.045
	Cr19-Ni23-Mo3-Cu3	19.00	22.86	3.05	2.98	0.045
	Cr19-Ni28-Mo3-Cu3	19.81	28.90	3.18	3.00	0.030
V	Cr23-Ni15-Mo3-Cu3	23.60	16.00	2.97	2.96	0.050
	Cr23-Ni28-Mo3-Cu3	24.25	28.35	3.24	3.02	0.020
VI	Cr27-Ni15-Mo3-Cu3	27.15	16.00	2.91	2.98	0.045
	Cr27-Ni23-Mo3-Cu3	27.20	23.85	2.91	3.05	0.045

chromium content from 5 to 19%, irrespective of the nickel content. The corrosion rate increases with higher chromium contents (23 and 27%), as is shown in the diagram. This increase of the corrosion rate may be associated with a two-phase austenite-ferrite structure. Nickel increases the corrosion resistance to a greater extent in steels with higher chromium contents than in low-chromium steels, which have predominantly a one-phase austenitic structure.



Variations of the corrosion rate of chromium-nickel-molybdenum-copper steel in denitrated sulfuric acid (76% H_2SO_4 and 0.05% HNO_3) at 130°, with the chromium and nickel contents. A) Corrosion rate (in $g/m^2 \cdot hour$), B) chromium content (%). Nickel content (%): 1) 15, 2) 19, 3) 23, 4) 28.

It may be assumed that the stability of low-carbon chromium-nickel-molybdenum-copper steels in denitrated sulfuric acid is determined by a definite chromium content (19-23%), and a one-phase austenitic structure, which is attained at a definite nickel content.

It must be pointed out, however, that at the highest corrosion resistance (3 mm/year), in tests in acid at 120-130° these steels are rated as materials of low resistance by the GOST 5272-50 scale. However, since the corrosion resistance of metals rises sharply with decrease of the temperature of the corrosive medium to 80° and lower, steels are then to be included among the resistant materials; this was demonstrated by the results of tests of experimental coolers under laboratory conditions [2].

The corrosion tests of these steels in denitrated sulfuric acid (at 130°) showed that decrease of the chromium content results in strong corrosion. This accounts for the more rapid destruction of welded joints in experimental coolers made from Cr18-Ni28-Mo3-Cu3 steel than in those made from Cr23-Ni23-Mo3-Cu3 steel as the welding heat at 600-800° produces structural changes

TABLE 2

Corrosion Rates of Chromium-Nickel-Molybdenum-Copper Steels in Denitrated Sulfuric Acid (76% H_2SO_4 and 0.05% HNO_3) at 130° (Duration of tests 300 hours)

Group	Steel grade	Corrosion rate (g/m ² ·hour)	Appearance of specimens after test (color and state of surface)
I	Cr5-Ni19-Mo3-Cu3	45.4	Golden lustrous; uneven, like orange peel
	Cr5-Ni23-Mo3-Cu3	38.2	
	Cr5-Ni28-Mo3-Cu3	55.2	
II	Cr9-Ni9-Mo3-Cu3	52.2	Golden, lustrous, smooth
	Cr9-Ni15-Mo3-Cu3	46.0	
	Cr9-Ni19-Mo3-Cu3	45.8	
	Cr9-Ni23-Mo3-Cu3	42.25	
	Cr9-Ni28-Mo3-Cu3	41.7	
III	Cr15-Ni9-Mo3-Cu3	12.9	Dull gray; smooth Dull gray; local pits
	Cr15-Ni15-Mo3-Cu3	35.5	
	Cr15-Ni19-Mo3-Cu3	16.9	
	Cr15-Ni23-Mo3-Cu3	8.65	
IV	Cr19-Ni9-Mo3-Cu3	4.08	Dull gray; smooth
	Cr19-Ni15-Mo3-Cu3	3.41	
	Cr19-Ni19-Mo3-Cu3	3.85	
	Cr19-Ni23-Mo3-Cu3	2.45	
	Cr19-Ni28-Mo3-Cu3	2.52	
V	Cr23-Ni15-Mo3-Cu3	8.1	Ditto
	Cr23-Ni28-Mo3-Cu3	4.66	
VI	Cr27-Ni15-Mo3-Cu3	26.4	Dull gray; local pits
	Cr27-Ni23-Mo3-Cu3	9.85	Dull gray; smooth

in these steels, with liberation of a carbide phase at the boundaries of the austenite grains, making the austenite in the boundary zone poorer in chromium.

In view of the fact that the degree of liberation of the carbide phase, and hence the impoverishment of the solid solution in chromium, depends on the amount of carbon present in the steel, the influence of carbon on the corrosion of Cr19-Ni28-Mo3-Cu3 and Cr23-Ni28-Mo3-Cu3 steels was tested under the conditions used for the tests described above.

The results of the corrosion tests on steels with different carbon contents are given in Table 3.

TABLE 3

Corrosion Rates of Cr19-Ni28-Mo3-Cu3 and Cr23-Ni28-Mo3-Cu3 Steels of Different Carbon Contents in Denitrated Sulfuric Acid (76% H_2SO_4 and 0.05% HNO_3) at 130° (Duration of tests 300 hours)

Steel	Carbon content (%)	Corrosion rate (g/m ² ·hour)	Appearance of specimens (color and surface)
Cr19-Ni28-Mo3-Cu3	0.10	14.8	Dark gray; rough
	0.20	16.2	
	0.27	26.7	
Cr23-Ni28-Mo3-Cu3	0.10	3.66	Gray; smooth
	0.30	9.53	Dark gray; rough

It is clear from these results that the corrosion rate of steels in denitrated sulfuric acid depends both on the carbon and on the chromium contents. The corrosion rate is almost doubled by an increase of the carbon content (from 0.10 to 0.30%). The absolute value of the corrosion is considerably higher with 19% than with 23% chromium. It follows that the carbon content of the steel should be the lowest possible (not over 0.06%), with a high chromium content.

It is also interesting to note the effect of copper on the corrosion resistance of steel under the same conditions. For example, the corrosion rate of Cr19-Ni28-Mo3 steel, without copper, is $33.2 \text{ g/m}^2 \cdot \text{hour}$, whereas the corrosion rate of the same steel containing 2% copper is $2.42 \text{ g/m}^2 \cdot \text{hour}$.

SUMMARY

1. The effects of chromium, nickel, and carbon on the corrosion of chromium-nickel-molybdenum-copper steels in denitrated sulfuric acid (76% H_2SO_4 and 0.05% HNO_3) at 130° were tested under production conditions in a sulfuric-acid plant; it was found that the corrosion of low-carbon chromium-nickel-molybdenum-copper steels with different contents of chromium (5-27%) and nickel (9-28%), but with constant contents of molybdenum(3%) and copper (3%) in works-denitrated sulfuric acid at $120\text{-}135^\circ$ depends mainly on the chromium content, and less on the nickel content.

2. The corrosion resistance of steel increases with increase of the chromium content from 5 to 19%, but decreases somewhat at higher chromium contents (23-27%). Nickel has much less influence on the corrosion of steel.

3. Carbon increases the corrosion of steel, this effect being greater at lower chromium contents. The carbon content of the steel should be as low as possible (not over 0.06%).

4. Chromium-nickel-molybdenum-copper steels containing 19-23% chromium and 9-28% nickel, being the most resistant to corrosion in denitrated sulfuric acid at 130° , may be recommended for use in experimental coolers, provided that the temperature of the cooler wall does not exceed 80° . For welded constructions without subsequent hardening, the steel should contain not less than 23% chromium.

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INFLUENCE OF THE NATURE OF THE SOLVENT ON THE KINETICS OF HYDROGENATION OF COTTONSEED OIL

D. V. Sokol'skii, L. S. Melekhina, and L. I. Perunova

In his earliest papers on the catalytic reduction of various organic compounds in the liquid phase, Fokin [1] drew attention to the decisive role of the solvent, and to the fact that sometimes hydrogenation can be effected only in certain solvents. The best solvents for hydrogenation of oleic, crotonic, and other acids in presence of platinum black were stated to be water, water-soluble acids and alcohols, ether, etc. Petroleum distillates, aromatic hydrocarbons, and higher alcohols and acids were classified as less suitable solvents.

Paal et al. [2] referred even earlier to the influence of the solvent on the reduction of nitrobenzene in presence of colloidal palladium in alcoholic and aqueous-alcoholic solutions.

Zal'kind and his associates [3] studied the influence of the solvent as well as the effect of the amount of catalyst on the hydrogenation rates of compounds with triple bonds (glycols). For example, it was shown that the reaction is slow in acetone and isobutyl alcohol; in water, ethyl alcohol, and methyl alcohol the hydrogenation-rate constants are 0.033, 0.044, and 0.60 respectively.

The solvent often determines the direction of a reaction, by influencing the ratio of the reaction products, if several different substances are formed in hydrogenation [4].

Taipale and his associates [5, 6] studied catalytic hydrogenation in various solvents. They investigated the hydrogenation rates of azines in various solvents (acetic acid, ethyl and methyl alcohols, ethyl acetate, ether). The hydrogenation rate of azines was highest in ethyl alcohol, less in methyl alcohol, and still less in ether.

The nature of the solvent was noted to influence the position of the boundary between the "diffusion" and "kinetic" regions of hydrogenation reactions in presence of Raney nickel [7].

However, the connection between the hydrogenation rates of organic compounds and the physicochemical properties of the solvents is not discussed in these papers.

Quite recently Antropov and Pochekaeva [8], in a study of the hydrogenation of allyl alcohol over platinum gauze at 25° in solvents with different dielectric constants (dioxane, acetic acid, ethyl and methyl alcohols, and various mixtures of dioxane with water and alcohol), found that the hydrogenation rate of allyl alcohol is highest in the solvent, the dielectric constant of which is close to that of the compound being hydrogenated. It was concluded that the hydrogenation rates of organic compounds on platinum, palladium, and probably nickel catalysts are functions of the dielectric constant of the solvent.

It has been shown by numerous experiments on hydrogenation of Raney nickel that the stability of the bonds between hydrogen and the catalyst surface depends to a considerable extent on the nature of the solvent and the pH of the medium [9, 10]. Some solvents increase the stability, others decrease it, and the ratio of the adsorbed and dissolved hydrogen varies accordingly. Therefore in the case of substances which are weakly adsorbed on the catalyst surface, such as ethylene derivatives, the primary influence of the solvent is manifested in variations of the bond energy between hydrogen and the surface [11].

In the present paper an attempt is made to correlate experimental facts observed in the hydrogenation of cottonseed and other oils in nonpolar and weakly polar solvents, with certain properties of the solvents.

In an earlier investigation [12] of the hydrogenation of cottonseed and linseed oils in benzene, toluene, and xylene solvents it was found that the hydrogenation rate at 50° is higher in toluene than in benzene, and higher in benzene than in xylene. At first sight it seems difficult to correlate this sequence of the influence of these solvents on the hydrogenation rate, with their nature or position in the homologous series. This fact prompted a more detailed study of the influence of these and other solvents on the hydrogenation rates of oils. The effect of temperature on the hydrogenation rates of vegetable oils in different solvents between 10 and 90° were studied, with the boiling point and vapor pressure of each solvent taken into account.

Good solvents for fats were chosen for the investigation. Solvents of "chemically pure" grade were mainly used. All the solvents were additionally purified by shaking in a current of hydrogen in presence of nickel catalyst obtained from very finely powdered nickel-aluminum alloy.

EXPERIMENTAL METHODS

The purified oils were hydrogenated in presence of a nickel catalyst made from 33% nickel-aluminum alloy; the apparatus and method were described previously [13, 14].

The experiments showed that the nature of the solvents has a considerable influence on the hydrogenation rate of oils.

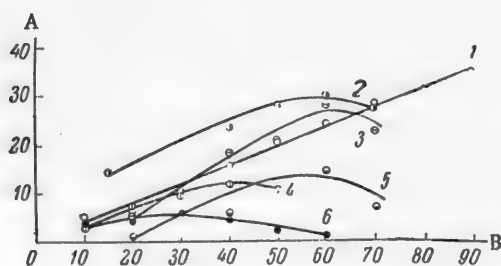


Fig. 1. Effect of temperature on the hydrogenation rate of cottonseed oil in various solvents. A) Average rate (ml/minute); B) temperature (°C). Solvents: 1) xylene, 2) toluene, 3) absolute alcohol, 4) acetone, 5) dioxane, 6) dichloroethane.

For each solvent studied, a definite temperature maximum was found at which the oil is hydrogenated at the greatest rate in that solvent. As this temperature is exceeded, the hydrogenation rate falls gradually but considerably.

Results obtained in the hydrogenation of linseed oil in benzene and toluene (Table 1), and of cottonseed oil in toluene, ethylbenzene, xylene, dioxane, alcohol, and acetone (Table 2, Fig. 1), are given below. Kinetic curves for the hydrogenation of cottonseed oil in xylene and absolute alcohol are given in Figs. 2 and 3.

The kinetic curves determined for hydrogenation of cottonseed oil under the optimum conditions for the particular solvents are given in Fig. 4. Curve 7 represents the hydrogenation of cottonseed oil without solvent at 50°. This is not the optimum temperature for the pure oil; the optimum is higher (about 150°) [15].

It follows from the data in Tables 1 and 2 that the optimum temperature for hydrogenation of the oil in benzene is 30°, and the optimum hydrogenation temperature increases proportionately with increasing boiling point when benzene homologs - toluene, xylene, or ethylbenzene - are used as solvents.

The optimum hydrogenation temperature is in the region of 60° both for linseed and for cottonseed oil, and it is therefore independent of the fatty-acid composition of the oil in this case. In ethylbenzene and xylene, cottonseed oil is hydrogenated at the maximum rate at 85 and 90° respectively.

Thus, for solvents of the benzene homologous series, similar in structure and physicochemical properties but differing considerably in their boiling points, the difference between the optimum hydrogenation temperature of cottonseed and linseed oils and the boiling point of the solvent is constant, about 50°. Increase of the boiling point of the solvent by 30° from one homolog to the next results in a corresponding displacement of the optimum hydrogenation temperature, also by 30°.

For comparison with solvents of the benzene series, dioxane and dichloroethane were also studied. Dioxane is of interest because it is a nonpolar solvent with a boiling point close to that of toluene, and is a good solvent for fats.

As was to be expected, the optimum temperatures for hydrogenation of oil in toluene and dioxane are similar. However, the hydrogenation rate in dioxane is lower than in toluene and the other solvents. In this case structural differences are probably predominant in their effect.

TABLE 1

Effect of Temperature on the Hydrogenation Rates of Linseed Oil in Benzene and Toluene (Amount of oil 1.86 g, of solvent 35 ml; catalyst from 2.0 g of Ni-Al alloy)

Solvent	Temperature (°C)	Maximum rate (in ml H ₂ /minute)	Half-hydrogenation time (minutes)	Total H ₂ absorbed (ml)
Benzene	9.5-10	10.8	39.0	191.5
	18-19	37.4	6.0	296.2
	30	55.7	4.0	299.2
	40	52.0	6.5	276.0
	50	46.0	7.5	258.4
Toluene	10.5	24.6	16.5	205.2
	20	36.4	7.8	260.3
	30	48.4	5.2	282.1
	40	55.7	4.4	283.2
	50	66.3	4.1	283.5
	60	80.9	3.0	300.6
	70	56.5	5.8	288.6

The hydrogenation rates of oils are even lower in dichloroethane and other chlorinated solvents. Dichloroethane is a good solvent for fats, and its boiling point is close to that of benzene. The hydrogenation rate of oil in dichloroethane reaches its maximum at 30°.

Absolute alcohol and acetone were used as the polar solvents for hydrogenation of oil (Table 2, Fig. 1). It is seen that the hydrogenation rate in alcohol is at its maximum at 60°. The optimum hydrogenation temperature in acetone is 40°.

It is seen that the hydrogenation optimum in alcohol and acetone is close to the boiling point of the solvent, i.e., the difference between the boiling point and the optimum hydrogenation temperature is much less than it is for nonpolar solvents. In acetone the hydrogenation rate is greatest at about 40°, although its boiling point is lower than that of, say, the nonpolar benzene, in which the optimum hydrogenation temperature is 30°. The polar ethyl alcohol and benzene have very similar boiling points, but the optimum hydrogenation temperature of oil in alcohol is 30° below that for benzene. In the case of acetone and alcohol, however, which have similar dielectric constants (21.5 and 25.8), the difference between the boiling point and the optimum hydrogenation temperature is similar, 16 and 18° respectively.

Very many investigations of the hydrogenation of unsaturated compounds in solvents have been reported. Many papers on the subject contain series in which solvents, differing greatly in their physicochemical nature, are arranged in some definite sequence according to the rate of hydrogenation of unsaturated compounds in them [3, 8]. In our opinion, such series cannot be always regarded as constant even for solvents similar in properties. For example, it is possible to obtain several different series, depending on the hydrogenation temperature, for the rates of hydrogenation of cottonseed oil in solvents of the benzene homologous series.

Therefore, by obtaining a series for the hydrogenation of unsaturated compounds in different solvents at a particular temperature, without a detailed investigation of the influence of temperature on the hydrogenation rate, it is possible to draw somewhat inaccurate conclusions concerning the influence of these solvents on the kinetics of the process.

For example, the conclusions drawn by Antropov and Pochekaeva [8] concerning the influence of the dielectric constant of the solvent (ethanol, methanol, acetic acid, dioxane, and water) on the rate of hydrogenation of allyl alcohol seem to be not quite correct from this standpoint. It is likely that these solvents, which were used by the above-named authors in the hydrogenation of allyl alcohol at room temperature, could be arranged in a different series if the hydrogenation is performed at another temperature. There is no doubt that the polarity of a solvent has a very important influence on the hydrogenation rate of unsaturated compounds,

TABLE 2

Hydrogenation of Cottonseed Oil in Nonpolar and Polar Solvents (Amount of oil 9.2 g, of solvent 25 ml; catalyst from 1.0 g of Ni-Al alloy)

Solvent	Temperature (°C)	Maximum rate (ln ml H ₂ /minute)	Average rate over 10 min. (ln ml/min.)	Half-hydrogenation time (minutes)	Total hydrogen absorbed (ml)	M. p. of hardened oil (°C)
Toluene	15	16.5	14.3	42	516.2	38.0
	40	26.2	23.2	25	730.4	61.0
	50	33.2	28.0	19	642.0	54.0
	60	34.9	29.9	17	600.0	46.5
	70	34.4	27.5	19	684.2	53.5
Xylene	10	6.7	5.0	—	191.0	28.5
	20	7.8	6.1	—	277.0	42.0
	30	11.8	10.3	60	519.0	44.5
	40	21.4	18.2	31	580.8	51.0
	50	24.5	20.2	26	625.0	51.2
	60	30.6	24.2	22	694.4	51.0
	70	33.9	28.5	20	638.6	45.0
	80	35.5	31.2	15	557.6	56.0
	90	41.7	34.9	14	705.0	
	100	Hydrogenation difficult				
Ethylbenzene*	20	1.5	—	—	40.0	
	30	9.2	6.4	—	192.0	
	40	12.0	8.7	62	243.2	
	50	15.0	11.0	50	280.0	
	60	19.5	16.5	21	370.2	
	70	27.7	21.8	12	372.2	
	80	37.0	25.3	7	400.6	
	90	31.7	24.6	9	425.0	
Dioxane	20	1.4	1.0	—	25.6	—
	40	6.3	5.7	—	257.6	—
	50	9.8	8.3	—	281.8	—
	60	17.1	14.5	—	329.0	—
	70	9.7	7.0	—	246.0	—
	80	Hydrogenation difficult				
Dichloroethane (1,2)	11	4.9	3.6	—	239.0	27.3
	20	5.1	3.9	—	236.8	28.0
	30	6.7	5.5	—	268.0	32.2
	40	6.0	4.1	—	212.0	25.0
	50	3.2	1.9	—	77.8	—
	60	2.1	1.0	—	24.8	—
Absolute alcohol	20	8.8	5.2	—	162.0	—
	30	10.6	8.8	—	383.0	42.2
	40	16.0	15.5	31	496.0	45.0
	50	20.2	19.2	26	511.0	46.3
	60	31.9	28.1	20	542.0	49.8
	70	26.8	23.1	30	440.5	38.2
Acetone	10	4.8	2.6	—	59.6	—
	20	8.9	6.6	—	366.4	29.6
	30	10.0	9.3	73	438.0	32.8
	40	15.7	11.6	55	466.3	35.8
	50	12.2	10.5	60	422.0	30.6

*4.6 g of oil was used for hydrogenation in ethylbenzene.

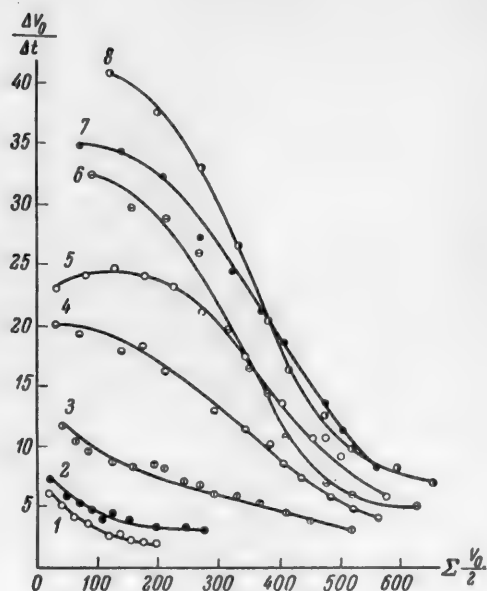


Fig. 2. Kinetic curves for hydrogenation of cottonseed oil in xylene. Temperature (°C): 1) 10, 2) 20, 3) 30, 4) 40, 5) 60, 6) 70, 7) 80, 8) 90.

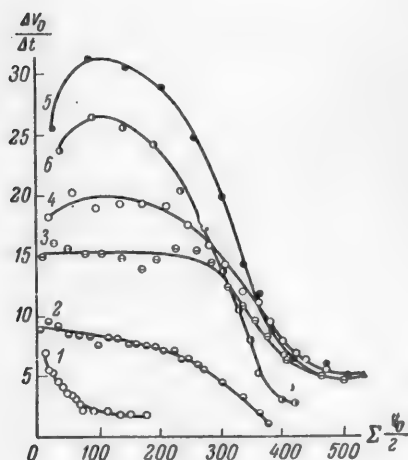


Fig. 3. Kinetic curves for hydrogenation of cottonseed oil in absolute alcohol. Temperature (°C): 1) 20, 2) 30, 3) 40, 4) 50, 5) 60, 6) 70.

but this rate is not a function of the polarity only. This may be illustrated by comparison of the hydrogenation of cottonseed oil in toluene and dioxane. The dielectric constants of toluene and dioxane are almost equal, but the hydrogenation rates of cottonseed oil in these solvents differ considerably.

In our studies of the hydrogenation of oils in solvents at different temperatures [12, 13] it was found that in the region of negative temperature coefficients, above the optimum temperature, the melting points of the hydrogenated oils are considerably lower than of the oils obtained at the optimum temperatures or below, with equal amounts of hydrogen absorbed. This suggests that the hydrogenation of oils above the optimum temperatures proceeds more selectively.

It is known that the selectivity of hydrogenation of oils depends on a number of factors, including the hydrogen pressure. The selectivity of the process increases with decreasing hydrogen pressure. We therefore calculated the partial pressures of hydrogen at the optimum temperatures, and the changes of partial pressure above the optimum temperatures, for solvents of the benzene homologous series and for the nonpolar solvent, dioxane. It was found, as is shown in Fig. 5 and Table 3, that the partial vapor pressures of benzene at 30-35°, of toluene and dioxane at 60-65°, and of xylene and ethylbenzene at 85-90° are almost equal, being all about 160±10 mm Hg. As the amount of hydrogen absorbed was measured in the gas buret under 1 atm. pressure, it follows that the hydrogen pressure was about 600 mm Hg. Therefore, this average value of the solvent vapor pressure, 160 mm, or the corresponding partial pressure of hydrogen, 600 mm, may be regarded as the limiting value, above which the reaction conforms to a hydrogen-diffusion mechanism.

Above the optimum temperatures the vapor pressures of these solvents increase considerably with each 10° increase of temperature. Increase of the solvent vapor pressure naturally leads to a reduction of the hydrogen partial pressure in the gas phase, and hence of the amount of hydrogen adsorbed on the catalyst surface, with a consequent considerable decrease of the hydrogenation rate.

Therefore, if the vapor pressure of a solvent at a given temperature is known, by making an appropriate correction for the concentration of the dissolved substance, it is possible to predict the hydrogen partial pressure which is suitable for hydrogenation in the given solvent.

In studies of the influence of solvents on the kinetics of hydrogenation of unsaturated compounds, the partial pressure of the solvent vapor must be taken into account.

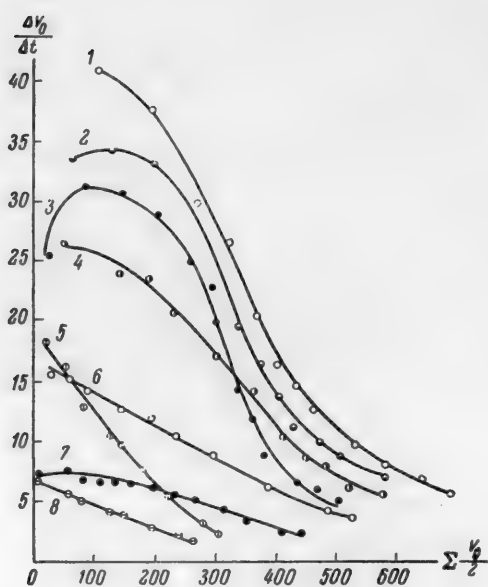


Fig. 4. Comparative data on the hydrogenation of cottonseed oil in different solvents at the optimum temperatures. Solvents and temperatures (°C) respectively: 1) Xylene, 90; 2) toluene, 60; 3) absolute alcohol, 60; 4) ligroline of b. p. 70-120°, 50; 5) dioxane, 60; 6) acetone, 40; 7) without solvent, 50; 8) dichloroethane, 30.

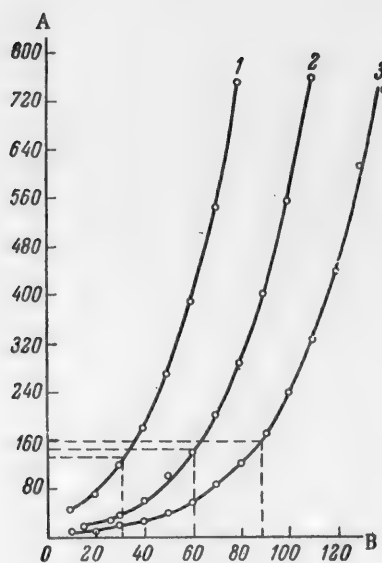


Fig. 5. Effect of temperature on the vapor pressure of solvents of the benzene homologous series. A) Vapor pressure (mm Hg), B) temperature (°C). Solvents: 1) Benzene, 2) toluene, 3) xylene.

TABLE 3

Optimum Hydrogenation Temperatures of Linseed and Cottonseed Oils and some Properties of Nonpolar Solvents

Solvent	B..p. of solvent (°C)	Dipole moment $\mu \cdot 10^{18}$	Optimum hydrogenation temperature (°C)	Vapor pressure at optimum temperature (mm Hg)
Benzene	80.1	0	30	150
Toluene	110.8	0.4	60-65	170
Ethylbenzene	136.2	0.6	80-85	170
Xylene	140	0-0.5	90	160
Dioxane	101.1	0.4	60	170
Dichloroethane	83.7	About 0	30	—

If suitable solvents are chosen, similar in their physicochemical characteristics, they can be utilized not merely as solvents but as substances which can vary the hydrogen partial pressure in the system at different temperatures, and thus increase the selectivity of the process.

SUMMARY

1. The effect of temperature on the hydrogenation rates of unsaturated compounds in various solvents was studied, and it was found that each solvent has a definite optimum hydrogenation temperature, which depends on the physicochemical properties of the solvent, and is determined primarily by the ratio of the solvent vapor and hydrogen pressures.

2. For nonpolar solvents a limiting vapor pressure was found, about 170 mm Hg; if this is exceeded, the hydrogenation rate is decreased because the process enters the "diffusion" region with respect to hydrogen.

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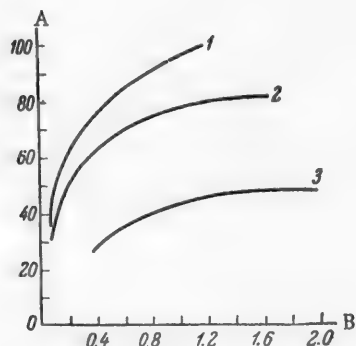
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PURIFICATION OF 8-METHYLTHEOBROMINE

E. S. Golovchinskaia, R. G. Glushkov, and A. A. Chemerisskaia

In an earlier communication, one of us [1] described a method for the methylation of 8-methylxanthine by dimethyl sulfate in aqueous alkali. The essence of this process is that the reaction is effected in two stages, and yields two products: 8-methyltheobromine, an intermediate substance in the synthesis of theobromine, in the first methylation stage, and methylcaffeine in the second. Together with 8-methyltheobromine, which is the main reaction product in the first stage, relatively small amounts of byproducts — methylcaffeine and 3,8-dimethylxanthine — are formed. The 8-methyltheobromine which crystallizes out of the reaction mixture always contains admixtures of these two compounds, which, being sparingly soluble in cold water, separate out together with the 8-methyltheobromine. Thorough separation, without losses, of these two methylated compounds from 8-methyltheobromine is a necessary prerequisite for the success of the synthesis as a whole, which depends on the complete utilization of all the other 8-methylxanthine derivatives in the second stage of the process.

A rational and simple method for the simultaneous separation of both methylcaffeine and 3,8-dimethylxanthine from 8-methyltheobromine was found as the result of a detailed study of the conditions for its separation from the reaction solution (after methylation) and from aqueous solution (after crystallization). This work involved determination of the solubilities of all three compounds in water at various temperatures (see Figure).^{*} 8-Methyltheobromine free from impurities was obtained by filtration of 8-methyltheobromine which crystallized out during the methylation, not from the cooled reaction mass as was always done in such cases, but at an elevated temperature (40–50°), followed by crystallization from water and filtration at the same temperature (i.e., at 40–50°). As the 8-methyltheobromine formed in the methylation conditions used contains only a small amount of 3,8-dimethylxanthine (6–7%), and the solubility of the latter in water rises very rapidly with even a small increase of temperature, it remains completely in the filtrates during two-fold separation of 8-methyltheobromine from large volumes of warm water.



Solubilities of methylated 8-methylxanthines in water. A) Temperature (°C), B) amount dissolved (in g/100 ml). 1) 3,8-Dimethylxanthine, 2) 8-methyltheobromine, 3) 8-methylcaffeine.

^{*} The solubilities were determined by F. E. Rabinovich in the Physical Chemistry Laboratory.

It is evident that all the methylcaffeine, which is the main impurity in 8-methyltheobromine, also remains in solution as it is sparingly soluble in cold water but very readily soluble on warming.

In addition to methylcaffeine and 3,8-dimethylxanthine, the warm aqueous solutions contain not less than 10% of the 8-methyltheobromine formed. This undesirable loss is, however, balanced by a corresponding increase of the yield of methylcaffeine, as the filtrate after separation of 8-methyltheobromine is used for further methylation in the second stage of the process, and all the dissolved partially methylated derivatives of 8-methylxanthine are then converted into methylcaffeine [1]. The 8-methylcaffeine isolated from warm solutions in this way has a high degree of purity and contains less than 1% of 3,8-dimethylxanthine or is entirely free from this impurity.

Searches for convenient methods for the purification of 8-methyltheobromine inevitably involved a search for a reliable method for determination of its purity, and for methods of qualitative and quantitative analysis of the impurities present. The reported melting point of 8-methyltheobromine (302-303°) [2] is in itself inadequate as even a qualitative characteristic of this substance, as its melting depends to a considerable extent on the rate of heating and on the temperature at which the capillary is introduced into the apparatus. Melting points were therefore determined in presence of a capillary containing the pure compound; this gave a fairly accurate idea of the quality of the substance obtained, and therefore of the efficiency of the purification method used (although inadequately purified 8-methyltheobromine sometimes melts simultaneously with the "standard"; its color and external appearance change considerably earlier).

The development of a method for quantitative determination of 3,8-dimethylxanthine in 8-methyltheobromine was primarily based on the observation that certain pyrimidine derivatives (mainly barbituric acid) can form colored complexes with salts of bivalent cobalt [3].

A study of the interaction of alkaline solutions of N-methyl derivatives of 8-methylxanthine with cobalt salts in aqueous solutions showed that the complexes are insufficiently stable in an aqueous medium. Precipitates were formed, which interfered with colorimetric determinations.

It was found in experiments with pure samples of 3,8-dimethylxanthine and 8-methyltheobromine that solutions of ammonium salts of these two methylated xanthines in absolute ethanol form fairly stable complexes, of different colors and readily soluble in alcohol, * with cobalt chloride - violet with 3,8-dimethylxanthine, and rose-yellow with 8-methyltheobromine. Investigations of synthetic mixtures containing various amounts (from 1 to 10%) of 3,8-dimethylxanthine confirmed that even small amounts of it produce a violet tinge in the pink solutions. Comparison of a large number of mixtures of different composition showed that the intensity of this tinge definitely corresponds to the amount of impurity present; this formed the basis of a colorimetric method for determination of 3,8-dimethylxanthine in 8-methyltheobromine. The method is based on successive visual comparisons of the color intensities of the solutions under test with two sets of standard solutions, containing 2, 4, 6 and 1, 3, 5, and 7% of 3,8-dimethylxanthine. For binary mixtures (8-methyltheobromine + 3,8-dimethylxanthine) this method is accurate to within 0.5-1%. If more than 1% of the possible third substance, methylcaffeine, is present, an additional reddish tinge is formed, which interferes with the results.

Investigation of a series of samples of 8-methyltheobromine, isolated from the reaction mass at 40-50° and crystallized once from water at the same temperature, showed that they did not contain more than 1% of methylcaffeine; this confirmed the practical suitability of the analytical method described. Nevertheless, we developed an alternative method for quantitative determination of methylcaffeine present in a mixture with 8-methyltheobromine and 3,8-dimethylxanthine, whereby it is possible to carry out a complete analysis of the reaction products which might be necessary if the methylation does not take the proper course. In this method a solution of a weighed sample of unpurified 8-methyltheobromine, or of a synthetic mixture, in dilute NaOH is extracted with chloroform, the solvent is driven off, and the residue is weighed. The 3,8-dimethylxanthine and 8-methyltheobromine remain in aqueous solution as the alkali salts.

EXPERIMENTAL METHODS

Isolation and crystallization of 8-methyltheobromine. 1) At the end of the methylation of a solution of 66.4 g of 90% 8-methylxanthine in 450 ml of 6% caustic soda solution (by addition of 70 ml of dimethyl sulfate, followed by simultaneous uniform additions of 16 ml of 42% caustic soda solution and 28 ml of dimethyl sulfate at pH 6.2 and 60°), the reaction mixture was stirred for 1 hour at 60°, warmed to 90-95°, and the hot solution was stirred for some time to decompose traces of dimethyl sulfate. The solution was then cooled to 45-50°, stirred for 1 hour at this temperature, filtered, and the crystalline mass was washed on the filter with a small amount of warm water. The pressed moist precipitate was crystallized from 600 ml of water containing charcoal. The filtered solution was cooled to 40-45°, kept 1 hour at that temperature, filtered, and washed with warm water. The weight of dry methyltheobromine with m. p. 301-303°, containing less than 1% of 3,8-dimethylxanthine, was 20.05 g, or 28.7% of the theoretical yield. The mother liquor from the crystallization of 8-methyltheobromine was cooled and filtered, and the precipitate was added to the filtrate for isolation of crude 8-methyltheobromine in the second methylation [1].

* To avoid the formation of precipitates in the preparation of barbiturate-cobalt complexes, Gomahr and Kresbach [3] recommended that the analysis should be carried out in absolute methanol in presence of piperidine, which aids the solution of the complexes in organic solvents.

2) A mixture of 20 g of pure 8-methyltheobromine with 5 g of methylcaffeine and 1 g of 3,8-dimethylxanthine was crystallized from 900 ml of water, the filtered solution was cooled at 45-50°, held at that temperature for 1 hour, filtered, and the precipitate was washed with a small amount of warm water. The weight of dry 8-methyltheobromine with m. p. 301-302°, free from methylcaffeine and containing less than 1% of 3,8-dimethylcaffeine by analysis, was 18.1 g, or 90.5% of the theoretical.

3) 20 g of 8-methyltheobromine of low melting point (it began to darken at 265°), containing 7% (i.e., 1.4 g) of 3,8-dimethylxanthine by analysis, was crystallized from 1400 ml of water. The hot filtrate was cooled at 50°, held for 1 hour at that temperature, filtered, and the residue was washed on a Buchner funnel with 25 ml of warm water (30-40°). The weight of dry 8-methyltheobromine was 14.5 g, m. p. 301-303°, the content of 3,8-dimethylxanthine was less than 1%. The yield was 77% of the theoretical.

Determination of 3,8-dimethylxanthine impurity in 8-methyltheobromine. The following solutions were prepared for the analysis: 1) 0.04% solution of pure 8-methyltheobromine in absolute ethyl alcohol; * 2) 0.04% solution of 3,8-dimethylxanthine, synthesized from 3-methyl-4-amino-5-acetylaminouracil [4], in absolute ethyl alcohol; 3) 0.28% solution of cobalt chloride (hexahydrate) in absolute ethyl alcohol; 4) 5% solution of ammonia in absolute methyl alcohol; 5) 0.04% solution of the sample to be analyzed.

Analytical procedure. 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 ml of 3,8-dimethylxanthine solution were put into seven dry test tubes of equal diameter, and the volume in each tube was brought up to 10 ml by addition of pure methyltheobromine solution. The eighth tube contained 10 ml of 8-methyltheobromine solution, and the ninth, 10 ml of the unknown solution. 0.9 ml of cobalt chloride ** solution was added to each tube, followed by 15 drops of ammonia. The ammonia was put first into the tubes with the standard solutions, in order of decreasing 3,8-dimethylxanthine content, and then into the tube with the unknown solution.

The solutions were shaken thoroughly, and after 15 minutes the color of the unknown solution was compared visually with the colors of the standards.

The solutions were examined vertically from above, with white paper placed under the tubes. The unknown solution was first compared with solutions containing 0, 2, 4, and 6% of 3,8-dimethylxanthine, and then with solutions containing 1, 3, 5, and 7%.

Determination of methylcaffeine impurity in methyltheobromine. An accurately weighed sample (about 0.4 g) was dissolved in 5 ml of 0.5 N NaOH solution in a small beaker, and the solution was transferred to a separating funnel. The beaker was rinsed with 2 ml of water. The solution was then shaken with 5 portions (5 ml each) of redistilled chloroform. The combined chloroform extracts were transferred to another separating funnel, washed with water (2 lots of 2 ml), dried over sodium sulfate, and filtered into a flask previously dried to constant weight and weighed. The residue after removal of the chloroform was dried in an oven at 80°.

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* The ethyl alcohol used must not contain over 0.2% water, as the presence of moisture causes turbidity which interferes with the color.

** The calculated amounts of cobalt salt should be used in the preparation of the solutions for analysis. If not enough Co⁺⁺ is present, the color is too weak, while an excess causes turbidity.

*** Original Russian pagination. See C.B. Translation.

REACTION OF BUTYL ORTHOTITANATE WITH FATTY ACIDS OF VEGETABLE OILS*

V. S. Kiselev and T. A. Ermolaeva

The literature contains only isolated references to the formation of titanium salts of fatty acids [1, 2] through titanium tetrachloride. The reaction of butyl orthotitanate with fatty acids of vegetable oils has not been described.

The purpose of the present work was to study the reaction of butyl orthotitanate with fatty acids of vegetable oils, and to obtain coatings based on the products.

EXPERIMENTAL METHODS

The oleic acid and butyl orthotitanate used for the work had the following characteristics. Oleic acid: boiling point 200-202° at 2-3 mm Hg; specific gravity 0.8985 at 20°; acid number 199 mg KOH; bromine number 59.1; refractive index 1.4630 at 20°; molecular weight (cryoscopic, in benzene) 282. Butyl orthotitanate: boiling point 161-162° at 2 mm Hg; refractive index 1.4910 at 20°; composition (%): C 53.78, H 10.45; Ti 14.06, O 21.71 (by difference).

The reaction between butyl orthotitanate and oleic acid was carried out in a four-necked flask fitted with a high-speed mechanical stirrer with an oil seal, a thermometer, a tube for supply of carbon dioxide, and an outlet tube connected to a graduated trap.

A stream of previously dried carbon dioxide was passed through the reaction flask in order that the butyl alcohol formed during the reaction should enter the graduated trap and not condense on the walls of the flask.

On the basis of preliminary experiments, the optimum temperature for the reaction between butyl orthotitanate and oleic acid was taken as 150°.

The rate and extent of the reaction were studied by variations of the amounts and sequence of addition of the starting materials.

The results (Fig. 1, 2) showed that the reaction rate depends on the amount of butyl orthotitanate present in the reaction mixture.

If the starting materials are put in together, the reaction proceeds at a high rate and is largely complete after 15-20 minutes.

If butyl orthotitanate is added stepwise (in 2-3 or more steps), the reaction is less rapid and less complete.

Moreover, with stepwise addition of butyl orthotitanate, small amounts of water as well as butyl alcohol are evolved.

If the starting materials are put in together, much less water is formed.

The reaction is more complete if the amount of oleic acid is increased to 6 moles per 1 mole of butyl orthotitanate.

*Communication III in the series on the production of titanium-containing film formers, and coatings based on them.

The liberation of small amounts of water together with butyl alcohol may be attributed to a reaction between butyl alcohol, formed in the reaction of oleic acid with butyl orthotitanate, and free oleic acid, with formation of butyl oleate.

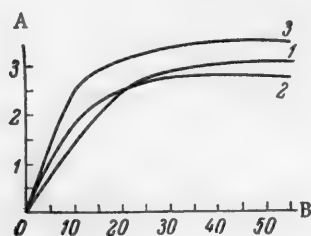


Fig. 1. Reaction of butyl orthotitanate with oleic acid. A) Amount of butanol formed (ml), B) time (minutes). Relative proportions (molar) of butyl orthotitanate and oleic acid: 1) 1:2, 2) 1:4, 3) 1:6.

oleic acid (Table 3). The results of these investigations show that when butyl orthotitanate reacts with oleic acid, polymeric products are formed, with complex, probably cyclic, structure, as the theoretical constants calculated for the formulas $Ti(OOCC_{17}H_{33})_4$; $(C_4H_9O)Ti(OOCC_{17}H_{33})_3$; $(C_{17}H_{33}COO)_3 Ti-O-Ti(OOCC_{17}H_{33})_3$, do not correspond to the values found for the substance isolated by molecular distillation.

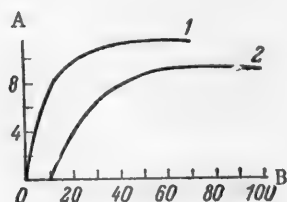
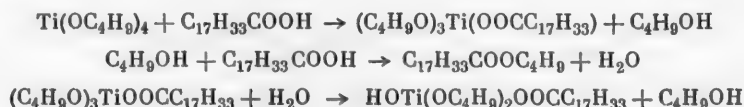


Fig. 2. Reaction of butyl orthotitanate with oleic acid. A) Amount of butanol formed (ml), B) time (minutes). Starting materials added: 1) Simultaneously, 2) stepwise.

When butyl orthotitanate reacts with oleic acid, 1 or 2 butoxy groups are substituted by oleate groups with liberation of butyl alcohol. The butyl alcohol immediately reacts with free oleic acid to form butyl oleate and water. Water hydrolyzes the butyl orthotitanate in which some of the butoxy groups have been replaced by oleate radicals. The hydrolysis is accompanied by condensation reactions leading to the formation of complex products.

The reactions which occur in the interaction of butyl orthotitanate with oleic acid may be represented by the following equations:



To determine their chemical composition, the reaction products of butyl orthotitanate and oleic acid were subjected to molecular distillation in a falling-film column.

Analysis of the fractions obtained by molecular distillation (Table 1) showed that the constants of the light fraction are close to the theoretical values for butyl oleate.

Analytical data for the residue from the molecular distillation (a thick tarry substance) are given in Table 2.

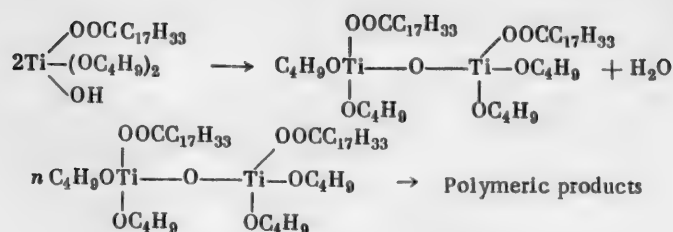
The substance isolated by saponification and decomposition of the residue, after molecular distillation of the reaction product of butyl orthotitanate and oleic acid, had constants close to the theoretical constants for

The suggestion that butyl orthotitanate polymers are formed, and are plasticized by oleic acid, is not justified, as in molecular distillation the free oleic acid would have been separated together with butyl oleate.

Moreover, if butyl orthotitanate polymers were present, a high content of butoxy groups should have been found; this was not the case.

The high acid number of the product may be attributed to decomposition of titanium oleate during the alkali titration, owing to the instability of the bonds between titanium and oleic acid residues.

The mechanism of the reaction between butyl orthotitanate and oleic acid may be represented as follows.



Film-Forming Properties of the Reaction Product of Butyl Orthotitanate and Oleic Acid

It was found in this investigation that the polymeric product formed by the interaction of butyl orthotitanate with oleic acid, which is a rather viscous thick resin (soluble in benzene, xylene, white spirit, butyl acetate, and amyl acetate; insoluble in alcohols and chlorinated hydrocarbons) has film-forming properties, and forms films which dry by the action of heat.

The presence of oleate radicals in the polymer molecules improves the adhesion and elasticity of the films formed, but decreases the film-forming properties of the polymer.

Whereas butyl orthotitanate forms films at room temperature [3], films based on the undistilled reaction product of butyl orthotitanate and oleic acid dry completely only at 160-170°.

TABLE 1

Molecular Distillation and Analysis of the Reaction Products of Butyl Orthotitanate and Oleic Acid

Conditions of molecular distillation					Analysis of products					
distillation No.	fractions	distillation temperature (°C)	residual pressure in system (mm Hg)	weight of fraction (%)	refractive index at 20°	acid number (mg KOH)	saponification number (mg KOH)	Ti content (%)	butoxy group content (%)	molecular wt., cryoscopic in benzene
1	Distillate	192—193	4.8 · 10 ⁻³	74.0	1.4550	0	169.0	0	—	342
	Residue	192—193		26.0	1.5210	188.9	251.5	11.4	2.6	1222
2	Distillate	145—146		66.3	1.4545	0	171.0	0	—	342
	Residue	145—146		33.7	1.5250	190.0	259.2	11.5	2.45	1326

Heat-dried films (2 hours at 150°) based on the substance isolated by molecular distillation are harder, but age and crack rapidly, whereas films made from the undistilled substance withstand 220-240° without loss of adhesion and elasticity.

Therefore the butyl oleate formed in a side reaction and present in the undistilled product acts as plasticizer in the reaction products of butyl orthotitanate and oleic acid, improving their adhesion and elasticity.

Study of the Processes Taking Place During Drying of the Reaction Product of Butyl Orthotitanate and Oleic Acid

The reactive groups in the reaction product of butyl orthotitanate and oleic acid, where further reactions leading to film formation may take place, are butoxy groups and double bonds in the oleate radicals. The film-drying process was studied from this standpoint.

TABLE 2

Elementary Composition of Residue after Molecular Distillation
No 2

Weight (g)	CO ₂ (g)	H ₂ O (g)	Ash (g)	Elementary composition (%)				
				C	H	ash	Ti	O (by difference)
3.79	9.09	3.76	0.73	65.45	11.00	19.26	11.55	12.00
6.51	15.65	6.35	1.25	65.6	11.91	19.05	11.52	11.97

TABLE 3

Analysis of the Acid Isolated by Saponification of the Residue
after Molecular Distillation

Constants	Calculated for oleic acid	Found in acid isolated
Acid number (mg KOH)	199.5	195.0
Bromine number (% of bromine added)	59.1	56.23
Refractive index at 20°	1.4638	1.4630
Molecular weight	282	279

TABLE 4

Analysis of Films Based on Titanium Oleate Polymer

Data	Residue after mole- cular distillation of Product No. 2, formed from 4 moles oleic acid and 1 mole of butyl orthotitanate	Film based on residue from molecular distillation
Ti content (%)	11.5	16.0
Butoxy group content (%)	2.45	0—1.0
Bromine number (% of added bromine)	55.5	27.5

As the films were insoluble in the usual solvents, analysis of them was difficult; for example, the molecular weight could not be determined. The other analyses were performed on suspensions of the films in solvents.

The results of determinations of butoxy group contents, double bonds from the percentage of added bromine, and percentage titanium contents, are given in Table 4.

The decreases of the bromine number and butoxy group content, accompanied by an increase of the percentage titanium content in the film, give an indication of the direction of the chemical processes taking place during the drying of the film.

The fact that film formation is completed only at high temperatures (150-160° and higher) indicates that polymerization and condensation processes (liberation of butyl alcohol and water, mutual saturation of double bonds, etc.), take place in the film.

The 50% decrease of the bromine number shows that double bonds take part in the film-forming process during heat drying.

The presence of titanium activates the double bonds in oleic acid and favors thermal polymerization.

The decrease of the butoxy group content during the drying of the films indicates that these groups are split off. However, as the butoxy group content of the starting substance is low, this cannot be the determining reaction.

The increase of the titanium content may be attributed to polycondensation processes, accompanied by removal of substances of low molecular weight such as water, butyl alcohol, etc.

It was found that atmospheric oxygen assists the drying of films based on the reaction products of butyl orthotitanate and oleic acid.

Films put in a vacuum thermostat under 20 mm residual pressure did not dry nearly as well as in an ordinary drying oven.

Reaction of Butyl Orthotitanate with other Fatty Acids from Vegetable Oils

Experiments on the reactions of butyl orthotitanate with mixtures of fatty acids isolated from sunflower, cottonseed, and castor oils were carried out as described above.

Products with film-forming properties were obtained in all cases.

Films obtained from the reaction products of vegetable-oil fatty acids with butyl orthotitanate have good gloss, good adhesion, and elasticity.

The films are fairly hard and can be used for coatings.

SUMMARY

1. Butyl orthotitanate reacts with oleic acid at 150°.
2. The formation of titanium oleate is accompanied by esterification with formation of butyl oleate, and hydrolysis and condensation of titanium compounds, leading to the formation of polymeric products.
3. Molecular distillation was used to isolate the polymeric reaction product of butyl orthotitanate and oleic acid; this has a complex, probably a cyclic structure.
4. The reaction products of butyl orthotitanate with oleic acid, and with mixtures of the fatty acids from sunflower, cottonseed, and castor oils, have film-forming properties and can be used as film-formers of a new type.

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FIBERS FROM SOLUTIONS OF LOW-SUBSTITUTED XANTHATES

E. A. Abramova, S. L. Munte, and N. K. Shemkov*

Cellulose xanthates obtained with a low consumption of carbon disulfide are of interest both with regard to their physicochemical properties and from a practical aspect, in relation to the formation of fibers from them.

Nikitin and Rudneva demonstrated in 1938-1939 [1] that cellulose xanthates, formed by the addition of 10-15% of carbon disulfide in the xanthation of alkali cellulose, can be obtained in solution. The solution of the fibrous xanthates in alkali was effected by the use of low temperatures, down to freezing.

Nikitin and Abramova [2] determined the conditions for preparation of filterable solutions of low-substituted xanthates, both from experimental celluloses of high reactivity, and for standard production pulps.

Filterable solutions of low-substituted xanthates (with addition of 10-15% of carbon disulfide, instead of the usual 38-40%) are made by the usual viscose process, with somewhat modified xanthation temperature conditions, and dissolved at low temperatures. The alkali cellulose is cooled to 4-5°, and is xanthated with 10-15% of carbon disulfide at the same temperature. These conditions ensure the maximum utilization of carbon disulfide for the main xanthation reaction, and reduce the loss of carbon disulfide in side reactions. The final xanthation temperature is 28-30°, and the total reaction time is 3 hours. The procedure for the preparation, shredding, and aging is determined according to the viscosity of the original cellulose.

For the dissolving of the xanthates in alkali below 0°, maximum swelling of the xanthate must be attained. The temperature must not decrease sharply during the first stage, as otherwise water crystallizes in the system, the alkali concentration increases, and the swelling effect is not obtained. During the second stage of dissolving, the substance is dispersed further at a lower temperature, and the dissolution of the product prepared by freezing is completed during thawing. When the gear pump is switched on, the solution temperature rises to 5-6° fairly rapidly.

This procedure was used for obtaining filterable xanthate solutions, containing 7.5-8% of α -cellulose and 7-7.2% of alkali, with 10 to 15% consumption of carbon disulfide (calculated on α -cellulose).

Solutions of low-substituted xanthates have high colloidochemical stability and low ripeness values [3]. The higher stability of these solutions is due to the temperature conditions used in their production, which minimize the formation of salts — destabilizers of viscose. In fact, repeated freezing and thawing of cellulose xanthate solutions increases their stability. In addition, the stability of the solutions depends on the caustic soda concentration and the ratio of the degree of substitution of the xanthate to the total alkalinity.

EXPERIMENTAL METHODS

Fiber formation. In the selection of spinning-bath compositions and spinning conditions, solutions of low-substituted xanthates cannot be regarded as ripened viscoses. It must be specially emphasized that these solutions have high colloidochemical stability, and their ripeness values do not characterize this stability. The spinning conditions of technical viscoses and solutions of low-substituted xanthates must be different. However, adequate theoretical bases for the choice of a spinning bath for a viscose of a definite composition are not yet available. This problem is usually solved empirically. The numerous existing patents on spinning-bath compositions are often mutually contradictory. No literature data at all are available on the spinning of ripe viscoses, which solutions of low-substituted xanthates formally are.

*The work was performed under the general guidance of Corresponding Member (AN SSSR) N. I. Nikitin, and with the help of Scientific Assistant L. A. Gorodetskaya, to whom the authors are deeply grateful.

The first experiments on the formation of fibers from solutions of low-substituted xanthates were carried out in an experimental spinning unit without bath circulation. The spinning-bath composition and spinning conditions were based on the results of Gorodetskii's experiments with viscoses after xanthation of alkali cellulose with 25% of carbon disulfide. Our solutions were obtained by xanthation with 10 and 15% of carbon disulfide from highly reactive experimental cellulose. Preliminary experiments showed that yarns of metric number 45-46 could be obtained in the first trials. The spinning proceeded continuously, without breaks. The physical properties of the yarn were poor.

In the next series of trials the viscose solutions were made from standard production pulp. The following conditions were adopted: mercerization 1.5 hours, alkali concentration 220 g/liter, temperature 19-20°. Press factor 2.5-2.6. Shredding for 3 hours at 35°. Aging for 17 hours from the start of mercerization, including 12 hours at 21-22°. Xanthation with 15% of carbon disulfide, with the alkali cellulose at 8-10°. Total xanthation time 3 hours, including 1.5 hours at 28°. The xanthates were dry, loose, deep yellow in color. The dissolving was carried out for 4 hours in a blade mixer.

In this series of experiments it proved possible for the first time to dissolve xanthates at -5°, which greatly simplifies the equipment necessary for the production of low-substituted xanthate solutions. The characteristics of the viscose solutions are given in Table 1. It follows from these results that viscoses made from standard pulp with 15% carbon disulfide have satisfactory filterability with the following composition (in %): α -cellulose 7.5-8, alkali 6.8-6.9.

With a dissolving temperature of -5°, the unfiltered viscoses had filtration "retardation" of the order of 140-170 seconds per 500 ml, and with -9 to -9.5°, 40-50 seconds per 500 ml. The solutions were spun by the one-bath process in a single-position spinning machine. The thread immersion length was 30-40 cm, without stretching, with two turns around the godet. The bath temperature was 45-46°, and the spinning was continuous, without breaks. The mechanical properties of the fibers are given in Table 2. The results show that, with a fairly low dry strength, the strength loss on wetting is normal. Fibers with good extensibility in the wet state were obtained from baths of high acid concentration and with increased zinc sulfate contents. Thus, the preliminary experiments showed that fibers of satisfactory strength properties can be obtained under definite spinning conditions. These results encouraged the continuation of work on the formation of fibers from solutions of low-substituted xanthates.

TABLE 1

Characteristics of Viscose Solutions Obtained with Consumption of 15% Carbon Disulfide

Shredding temp. alkali cellulose (°C)		Temp. of alkali cellulose before xanthation (°C)	Dissolving temperature (°C)		Analysis of viscose solution					Filtration procedure	"Retardation" of filtration of the filtered viscose (seconds)
initial	final		alkali solution	final	viscosity (sec.)	ripeness (ml HNCl)	"Retardation" of filtration of unfiltered solution (sec.)	contents (%)			
								α -cellulose	alkali		
30	36	10	0	—8.7	68	8.5	170/500	7.5	7.06	Normal	0
23	35	10	2	—9	42	7.2	43/500	7.5	6.83		2
26	35	11	1.5	—9	55	6.5	43/500	7.8	6.97		0
33	35	9	0	—5	48	8.4	140/500	7.4	7.02		3
34	36	9.5	0	—5	44	6.7	137/500	7.3	6.55		2.5
33	35	10	1	—9.8	37	7.6	50/500	7.5	6.63		0.6
19	19	8	0	—5	60	7.5	104/500	7.93	6.83		0
22	20	9	1.5	—5	43	6.8	62/500	7.92	6.72		0

TABLE 2

Mechanical Properties of the Yarn

Ripeness (ml HN_2Cl)	Viscosity (sec.)	Bath composition (g/liter)			Bath tempera- ture ($^{\circ}\text{C}$)	Spinning speed (m/min.)	Metric number of fiber	Breaking length (km)		Elongation (%)		Number of filaments
		H_2SO_4	Na_2SO_4	ZnSO_4				dry	wet	dry	wet	
7.3	30	128.3	302	52.5	45	45	35.7	11.1	3.9	24.9	39.3	40
7.3	30	128.3	302	52.5	45	45	35.1	12.8	4.3	25.1	37.9	40
7.6	33.6	128.3	302	52.5	45	45	33.3	13.4	5.4	26.5	43.8	40
7.3	45	131.0	303.4	53.1	46	45	35.0	11.3	3.4	21.1	29.3	40
7.95	31	101	303	22	45	45	38.2	10.7	3.1	17.8	24.2	40
7.3	39	109.7	275	48.5	45	45	35.4	12.3	4.3	23.9	36.3	40
7.6	33.6	95	275	48.5	46	45	35.6	12.3	3.7	22.8	33.6	40

Spinning of staple fiber. Viscose solutions with the consumption of 15% of carbon disulfide were made from three industrial pulps. Production alkali cellulose, previously cooled to 7-8 $^{\circ}$, was used for xanthation. The xanthate was dissolved in a portable mixer installed in the refrigeration unit of the works.

Several experiments on xanthation of alkali cellulose with 10% of carbon disulfide gave positive results; the filtration of the viscoses took 5-10 minutes longer than the filtration of solutions made with 15% carbon disulfide. Twenty-four batches were spun from the viscose solutions. The spinning was performed on one side of a two-position reel-spinning machine, with bath circulation. The solutions used for the spinning had the following characteristics:

α -Cellulose 7.8-8.2%
 Caustic soda 6.8-7%
 Ball-fall viscosity 35-60 sec.
 NH_4Cl ripeness 6-7.5.

The spinning conditions were varied; spinnerets with 3600 0.08 mm holes, 600 0.08 mm holes, and 2400 0.06 mm holes were used. The immersion length in the bath was 67-82 and 26-34 cm. The bath temperature was 46-50 $^{\circ}$, and the spinning speed was 57.8 m/minute. The stretch at the spinneret was 166, 126, and 117%. The fibers were finished in skein form in the finishing section, by the production process.

Stable spinning was not achieved with 3600-hole spinnerets (with pump feed 390 cc/minute). The fibers had breaking length 13-14 km, and 28-30% dry extensibility. Spinning was stable with 600-hole spinnerets, with the viscose pumping rate reduced to 70-77 cc/minute. When the spinning conditions and bath composition were being chosen, it was found that fibers of better mechanical properties are obtained with 128-130 g sulfuric acid per liter and a higher sulfate content in the bath. Fibers spun in baths of the same acid content but a lower sulfate content are weaker. Spinning below 45 $^{\circ}$ also gave fibers of inferior properties. The length of the arc of contact of the thread with the spreading and directing rollers in the bath, and the immersion depth of the latter, are of definite significance. As the resistance to friction increases, the stretch of the thread in spinning becomes greater, and the mechanical properties of the fibers improve.

The spinning conditions and the properties of the fibers are given in Table 3. The most favorable spinning conditions for low-substituted xanthate solutions, giving fibers of normal breaking length, 16-18.4 km, were tentatively established; spinning speed 58.7 m/minute with spinnerets with 600 0.08 cm holes, bath temperature 48-50 $^{\circ}$, thread immersion length 69-78 cm, spinning stretch 126%. Spinning bath composition (in g/liter): H_2SO_4 130-140, Na_2SO_4 350-375, ZnSO_4 17-18.5.

In addition to the experiments described above, trials were carried out on the spinning of fibers with 33% plastic stretching. Despite the fact that the spinning conditions and bath compositions were not chosen specially in this case, the fibers obtained had satisfactory mechanical properties.

TABLE 3

Spinning Conditions and Mechanical Properties of Staple Fiber (Carbon disulfide consumption 15%)

Ripeness (ml HN ₂ Cl)	Viscosity (sec.)	Bath composition (g/liter)			Sp-gr. of bath	Bath temperature (°C)	Thread immersion length (cm)	Holes in spinneret	Spinning speed (m/minute)	Spinning stretch	Metric number of fiber	Breaking length in dry state (km)	Elongation (%)
		H ₂ SO ₄	Na ₂ SO ₄	ZnSO ₄									
6.1	38	122	343	18.1	1.336	48—50	74	600	58.7	126	4196	16.8	21.6
5.8	45	125	314	15.2	1.304	46—48	74	600	58.7	126	4141	16.0	21.3
5.8	45	125	314	15.2	1.304	46—48	72	600	58.7	126	4034	15.0	19.7
6.1	58	135	357	18.7	1.362	47—48	69	600	58.7	126	4163	16.0	23.3
6.1	58	135	357	18.7	1.362	47—48	69	600	58.7	126	3968	16.6	28.6
6.1	58	135	357	18.7	1.362	47—48	67	600	58.7	126	4234	17.2	23.3
6.7	30	137	360	17.1	1.362	48	69	600	58.7	126	3058	16.2	22.0
6.7	30	137	360	17.1	1.362	48	71	600	58.7	126	4632	16.0	21.0
6.7	30	137	360	17.1	1.362	48	74	600	58.7	126	4346	16.9	23.3
6.7	30	137	360	17.1	1.362	48	78	600	58.7	126	4960	17.4	18.0
6.7	30	137	360	17.1	1.362	48	71	600	58.7	126	4746	18.4	20.0
6.5	45	140	376	16.8	1.378	48—50	69	600	58.7	126	3988	18.3	28.3

SUMMARY

Filterable viscose solutions were obtained from several industrial pulps with additions of 10 and 15% carbon disulfide in an experimental unit. The xanthates are dissolved in alkali at -5 to -6°. It was shown that fibers can be spun from solutions of the low-substituted xanthates.

Tentative conditions for the spinning of staple fibers with satisfactory strength characteristics were established.

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A STUDY OF THE CHEMICAL PROPERTIES OF DIOXANE LIGNIN FROM OAK AND CERTAIN CONIFERS

M. M. Chochieva and N. I. Nikitin

The present investigation consisted of a study of the chemical composition of oak wood in relation to the type of forest, and a study of the properties of woods from the Far East.

Specimens of wood from the oak (*Q. fontinalis*) from the Tellerman forest plantation (aged 60-75 years), *Picea ajanensis* from the Dolinskii region of Sakhalin (63 years), *Abies nephrolepis* from the fir plantation in the Tsikhuma river basin of the Shkotova plateau (92 years), and *Abies sachalinensis* from the Dolinskii region of Sakhalin (50 years) were used in the investigation.

For isolation of the lignin, the wood was freed from ether- and water-soluble substances and extracted with dioxane in presence of 0.1% HCl as catalyst.

The choice of dioxane as solvent for lignin was determined by its neutral character, its moderate boiling point (101.4°), and its power to dissolve many aromatic substances, including phenols, but not cellulose. Wood carbohydrates and simple sugars [1] (mannose, fructose, xylose, arabinose) do not form humus substances when heated in dioxane in presence of 0.1% HCl. Therefore the small amount of acid which must be added for the reaction acts only as a catalyst. It was shown with the use of radioactive (C^{14}) dioxane that dioxane lignin contains almost no dioxane. Moreover, dioxane itself does not decompose when heated with 0.12% HCl without wood.

The object of the work was a comparative study of the chemical composition of dioxane lignin from the above-named woods, and determination of the effects of different amounts of moisture on the yields of dioxane lignin during its extraction.

EXPERIMENTAL METHODS

To determine the influence of moisture on the amount of lignin extracted, oak wood sawdust dried at 105° to constant weight was fractionally extracted with dry dioxane acidified with gaseous hydrogen chloride. The weight of dioxane was ten times the weight of the wood, and the HCl concentration was 0.1%. The extraction was performed on the water bath for 32 hours, with the solvent changed every four hours. The dioxane solution was filtered to remove the sawdust, and the solution was poured into dry ether with stirring to precipitate lignin. The total yield of dioxane lignin was 9.0% on the weight of the original wood. During the first 12 hours only 4.1% lignin was extracted (Table 1).

Air-dry wood was used in the subsequent experiments. The dioxane was acidified by addition of concentrated HCl.

The yields of dioxane lignin were higher in the extraction of air-dry wood with dioxane. For example, fractional extraction of air-dry oak wood (with solvent changed every 4 hours) yielded 6.2% of lignin in 12 hours, as compared with 4.1% from absolutely dry wood. The hygroscopic moisture present in the wood probably assists hydrolysis of the bonds between lignin and carbohydrates, so that the extraction of lignin is more complete.

The yield of dioxane lignin increased with increase of the extraction time.

TABLE 1

Yields of Dioxane Lignin from Different Woods and Under Different Extraction Conditions

Starting material*	Experimental conditions			Yield of "crude" dioxane lignin (%)	
	moisture (%)	concentration (%)	extraction time (hours)	on weight of wood taken	on original wood
Oak, original absolutely dry wood	0	0.09	12	4.5	4.1
Oak, original absolutely dry wood	0	0.09	32	9.9	9.0
Oak, original air-dry wood	7.4	0.09	12	6.8	6.2
Oak, original air-dry wood	8.3	0.13	14	7.7	7.0
	8.4	0.13	20	16.1 } 17.3 18.5	15.7
	10.0	0.11	28		
Oak, original air-dry wood, fractional extraction	8.9	0.13	28	25.1	22.7
Abies nephrolepis, original air-dry wood	9.3	0.10	28	14.6	14.2
Abies sachalinensis, original air-dry wood	8.7	0.10	28	16.1	15.2
Picea ajanensis, original air-dry wood	9.5	0.13	28	23.8	22.1

*Sawdust after extraction with ether and with water.

Increase of the moisture content of the oak sawdust above the air-dry level did not show any regular changes in the yields of dioxane lignin.

The following extraction conditions were adopted as the result of these experiments: the air-dry sawdust previously extracted with ether and hot water, was heated with an eight-fold quantity of dioxane in presence of 0.10-0.13% HCl in a flask fitted with a reflux condenser, for 28 hours on a boiling water bath. The filtered brown dioxane solution was evaporated under vacuum to a small volume (40-50 cc) and the solution was poured in a thin stream with stirring into dry ether to precipitate the lignin. The pale-colored precipitate of "crude" dioxane lignin was filtered off, washed with ether, and dried first in a vacuum desiccator at room temperature, and then in a vacuum drying oven at 50-60°.

When the crude product was left exposed to air, it darkened in isolated patches, probably owing to oxidation or condensation; this indicates considerable variability of the substance.

It follows from the data in Table 1 that the highest yield of "crude" dioxane lignin (22.7% on the original wood) was obtained by fractional extraction (with solvent changed every 7 hours) of air-dry wood for 28 hours. Most of the lignin (12.2%) was dissolved during the first 7 hours, and 6.3, 2.7, and 1.5% on the weight of the original wood were extracted during the subsequent stages.

The behavior of different conifer woods* in dioxane extraction by the above method varied; this was probably determined by the specific characteristics of each kind of wood.

The highest yield of "crude" dioxane lignin was obtained from *Picea ajanensis* wood (22.1% on the original wood). Further extraction increased the yield of dioxane lignin only slightly.

It must be pointed out that dioxane in presence of 0.1% HCl extracted only about 3/4 of the lignin present in the original wood. The rest (about 1/4) remained in the wood. Investigation of the chemical composition of the wood residues showed that a considerable proportion of hemicelluloses (73.2% of the total

* The yields of sulfuric-acid lignin (in % on the original wood) from these woods were: *Picea ajanensis* 28.7, *Abies nephrolepis* 30.6, *Abies sachalinensis* 28.4, oak 22.3.

hemicellulose content of oak, and 81.9% of *Picea ajanensis*) went into dioxane solution together with lignin. Cellulose was not affected by the dioxane extraction. The chemical composition of the "crude" dioxane lignin from the above-named woods, and its variations after boiling with distilled water, were determined by the methods used previously [3, 4]; hydroxyl groups were determined by the Verley and Bölsing method [5]. The results of chemical analysis (mean values of two or more parallel determinations) of "crude" dioxane lignin are given in Table 2.

TABLE 2

Comparative Composition of "Crude" Dioxane Lignin from Different Woods

Constituents	Oak		Picea ajanensis		Abies nephrolepis		Abies sachalinensis	
	% on							
	weight of "crude" dioxane lignin	original wood	weight of "crude" dioxane lignin	original wood	weight of "crude" dioxane lignin	original wood	weight of "crude" dioxane lignin	original wood
Elementary composition { C H	56.34 5.56	— —	58.03 5.95	— —	59.25 6.13	— —	57.85 6.01	— —
Methoxyl groups	14.7	2.3	12.0	2.7	13.6	1.9	13.0	2.0
Hydroxyl groups	10.4	1.6	13.7	3.0	11.9	1.7	12.7	1.9
Pentosans with correction for uronic acids	26.2	4.1	5.3	1.2	5.7	0.8	5.3	0.8
Mannan	Nil	Nil	4.8	1.1	4.9	0.7	6.4	1.0
Uronic acids	8.3	1.3	3.4	0.8	5.1	0.7	5.2	0.8
Total { carbohydrates pure dioxane lignin	34.5	5.4	13.5	3.1	15.7	2.2	16.9	2.6
	65.5	10.3	86.5	19.0	84.3	12.0	83.1	12.6
Solubility in hot water	83.2	5.2	84.8	7.7	39.7	4.2	34.4	5.2

It follows from Table 2 that "crude" dioxane lignin extracted from these woods was closer in its C, H and OCH₃ contents to lignin isolated by acid methods than to carbohydrates (cellulose contains 44.4% C and 6.2% H). This was also reported in earlier papers [6, 7]. Owing to the presence of considerable amounts of carbohydrates (from 13.5 to 34.5%)* in "crude" dioxane lignin, its carbon and OCH₃ contents were lower than those of lignins extracted by means of concentrated acids. It must be added that when dioxane lignin was treated with concentrated sulfuric acid, its elementary composition and methoxyl content became the same as those of sulfuric-acid lignin extracted directly from wood.**

When "crude" lignin was boiled with distilled water (5 hours, 1/30 liquor ratio), about 1/3 went into aqueous solution.

The external appearance of "crude" dioxane lignin was greatly altered by treatment with boiling water. The yellowish pink "crude" lignin became dark when heated with water. It floated in the form of a tarry substance on the liquid surface, and solidified to a dark brown mass on cooling.

The chemical composition of dioxane lignin was also greatly changed after treatment with hot water, as Table 3 shows.

The table shows that the elementary composition of the lignin after treatment with boiling water became very close to the elementary composition of the sulfuric-acid lignin from all four woods. The methoxyl group contents also increased considerably after the treatment with hot water, approaching the contents in sulfuric-acid lignin.

* This was 1/7 of the total hemicellulose content of conifers and 1/5 of oak respectively.

** For example, after dioxane lignin from oak was treated with 64% H₂SO₄, the residue contained only 65.4% lignin, containing 20.1% OCH₃, 62.65% C and 5.30% H.

All three conifer woods are characterized by complete removal of mannan from the "crude" dioxane lignin as the result of water extraction.

Comparison of Tables 2 and 3 shows that half the uronic acid contents of three of the lignins were removed by hot-water treatment; they were extracted completely from *Picea ajanensis* lignin.

TABLE 3

Composition of Dioxane Lignin Treated with Hot Water, and Sulfuric-Acid Lignin from Different Woods (% of absolutely dry wood)

Substance	Oak		Picea ajanensis		Abies nephrolepis		Abies sachalinensis	
	dioxane lignin		dioxane lignin		dioxane lignin		dioxane lignin	
	on wt. of lignin taken	original wood	on wt. of lignin taken	original wood	on wt. of lignin taken	original wood	on wt. of lignin taken	original wood
Elementary composition {C H	60.67 5.51	60.62 5.44	61.60 5.68	64.23 5.78	63.87 5.13	63.80 5.77	62.67 5.67	64.64 5.76
Methoxyl groups	19.0	1.9	20.8	14.8	2.1	15.6	1.6	16.6
Hydroxyl groups	8.8	0.8	9.0	9.0	1.3	—	9.9	1.0
Pentosans with correction for uronic acids	12.1	1.2	1.6	1.3	0.2	—	0.7	0.1
Mannan	—	—	—	Nil	Nil	Traces	Nil	—
Uronic acids	6.0	0.6	1.2	Nil	Nil	3.1	0.3	—
Total {carbohydrates pure lignin	18.1	1.8	2.8	1.3	0.2	3.8	0.4	—
	81.9	8.7	97.2	98.7	14.2	96.2	9.6	—

The fractions of pentosans extracted from dioxane lignins were 2/3 in the case of oak, 5/6 in the case of *Picea ajanensis*, and 7/8 in the case of the *Abies* species. This suggests that in oak, *Abies sachalinensis*, and *Abies nephrolepis* the uronic acids are bound more firmly to the lignin than are pentosans and especially hexosans.

Therefore the dioxane lignin from the deciduous and coniferous species studied is a lignin-carbohydrate complex. The lignin-carbohydrate ratio in this complex varies according to the species. The dioxane lignin extracted from coniferous woods had a lower carbohydrate content (13.5-16.9%). Hence the amount of pure lignin in the complex was 83.1-86.5%. Oak lignin was more contaminated with carbohydrates. It contained only 65.5% pure lignin and 34.5% carbohydrates.

A part of the carbohydrates was extracted from the lignin-carbohydrate complex by boiling water, the removal of carbohydrates being more complete from dioxane lignin of conifers. For example, in the case of *Picea ajanensis* 2.9% of carbohydrates (calculated on the original wood), or 93.6% of the total carbohydrate content of the lignin, was extracted by boiling water from the "crude" dioxane lignin. In the case of oak, extraction of the "crude" dioxane lignin in boiling water removed 3.6% of hydrocarbons (on the original wood), or 66.7% of the carbohydrates present.

Certain peculiarities of dioxane lignin from *Picea ajanensis*, such as its high yield, greater purity, and higher solubility in hot water, are apparently due to the properties of this wood itself, which have been studied little as yet.

To establish the aromatic nature of the lignin, mild oxidation of both the native lignin (in the wood) and of the isolated lignin was carried out by means of nitrobenzene in an alkaline medium.

The oxidation was performed by Freudenberg's method [8], the aldehydes being determined as the 2,4-dinitrophenylhydrazones of vanillin and syringaldehyde[9].

The results of the oxidation of oak and *Picea ajanensis* woods are given in Table 4.

It follows from Table 4 that in the oxidation of oak wood the maximum yield of aromatic aldehydes, 44.9% (calculated on the lignin) was obtained at 160° in 8% NaOH. The aldehyde yield decreased when the alkali concentration was lowered to 4%.

The best oxidation conditions for the wood of *Picea ajanensis* were 160° and 3.4% alkali. 22.8% of vanillin was obtained under these conditions. These yields of aldehydes are very close to the results reported by other authors. Hibbert obtained 47.2% aldehydes in the oxidation of red oak wood, and oxidation of wood of the common spruce yielded 25.0% of vanillin [8].

TABLE 4

Results of Oxidation of Wood with Alkaline Nitrobenzene

Type of wood	Experimental conditions		Yield of aldehydes (% on pure lignin)	Properties of aldehyde hydrazones	
	oxidation temperature (°C)	NaOH concentration (%)		OCH ₃ (%)	melting point (°C)
Oak wood, original*	160	8	44.9	15.38	219—220
	150	8	37.3	15.35	218—219
	160	4	15.3		
<i>Picea ajanensis</i> wood, original*	160	3.4	22.8	9.35	251—252
	150	3.4	22.4	9.33	250—251
	150	8	17.6	9.06	
Ditto, after heating for 28 hours with 0.1% HCl	160	3.4	24.7	9.34	250—252

* Sawdust after extraction with ether and water.

Oxidation of the wood of *Picea ajanensis*, previously heated on a boiling water bath with 0.1% HCl for 28 hours (conditions for the extraction of dioxane lignin), yielded 24.7% of vanillin. This shows that a weakly acid medium favors splitting of the bonds between lignin and carbohydrates, so that somewhat higher yields of aromatic aldehydes are obtained.

When "crude" dioxane lignin isolated by the mild method from oak was oxidized by alkaline nitrobenzene under the same conditions, the yield of aromatic aldehydes was only 22.7% on the weight of the pure lignin (without carbohydrates), which is half the yield of aldehydes obtained by direct oxidation of wood (Table 5).

The oxidation of "crude" dioxane lignin from *Picea ajanensis* yielded only 4.6% of vanillin, or about 1/5 of the quantity obtained by direct oxidation of the wood (22.8%).

Control experiments on the oxidation of pure vanillin under the same conditions showed that vanillin is not decomposed in this process. At 150° 99.4% of the original vanillin was recovered.

The explanation for the low yield of aromatic aldehydes in the oxidation of dioxane lignin isolated by a mild method is that in this case the oxidation takes place in solution (in contrast to the oxidation of wood), and therefore the decomposition of lignin proceeds either too far, or not in the direction which leads to the formation of vanillin. It is probable that in addition to vanillin, some other products are formed, which cannot be determined by means of 2,4-dinitrophenylhydrazine.

To study the decomposition of dioxane lignin by the action of pure alkali alone, "crude" dioxane from oak was heated under the conditions of oxidation with alkaline nitrobenzene (at 150° for 3 hours with 8.3% NaOH), but without the oxidizing agent (nitrobenzene). The lignin combined with a considerable amount of

NaOH, 33.6% on the weight of the lignin, during the reaction. This is evidence of the formation of a large number of acid groups in the lignin. The loss of lignin substance, which was determined by reprecipitation of lignin by addition of acid, was 49.4% (on the weight of the original "crude" dioxane lignin).

These results confirm the hypothesis that when soluble dioxane lignin is oxidized by nitrobenzene in an alkaline medium, the oxidation reaction goes far deeper, leading to breakdown of the lignin with formation of acid products, the nature of which is not yet known.

According to our calculation, the methoxyl group content of the hydrazones obtained from the mixed aldehydes formed in the oxidation of oak wood and dioxane lignin (15.3% on the average) corresponds to a 3:1 ratio of syringaldehyde to vanillin.

TABLE 5

Results of Oxidation of "Crude" Dioxane Lignin with Alkaline Nitrobenzene

Substance oxidized	Experimental conditions		Yield of aldehydes (% of pure lignin)	Properties of aldehyde hydrazones	
	oxidation temperature (°C)	NaOH concentration (%)		OCH ₃ (%)	melting point (°C)
Oak dioxane lignin, "crude" {	160	8	22.7	15.3	216—217
	150	8	16.3	15.3	215—216
Picea ajanensis dioxane lignin, "crude" {	160	8	4.2	9.2	248—249
	150	3.4	4.6	9.3	248—249
Vanillin {	160	8	83.7	9.3	256—258
	150	8	99.4	—	251—252

It is known that in the oxidation of lignins by alkaline nitrobenzene, in which the lignins are isolated from the wood by different methods, the yields of aromatic aldehydes are considerably lower than in oxidation of the wood itself. Thus, in the oxidation by alkaline nitrobenzene of alcohol-soluble blolignin, formed in the destruction of spruce wood by the fungus *Coniophora cerebella*, only 8.9% of vanillin was obtained (as against 21.8% in the oxidation of wood); alkali lignin from spruce [11] gave 13.7%, highly condensed sulfur-acid lignin gave 1.5%, and cuprammonium lignin gave 17.2% of vanillin.

The lower yields of aromatic aldehydes can probably be ascribed to differences in the degree of alkaline decomposition [12] of the isolated lignins, in which acid products are formed in addition to aromatic aldehydes [13].

SUMMARY

1. In a study of lignins from different species, experiments were carried out on the extraction of lignin from the woods of oak, *Picea ajanensis*, *Abies nephrolepis*, and *Abies sachalinensis*, by means of dioxane in presence of 0.1–0.13% hydrochloric acid. Higher yields of dioxane lignin were obtained from air-dry than from absolutely dry oak wood.

2. The "crude" lignin precipitated from dioxane by means of ether, in yields from 14.2% (*Abies nephrolepis*) to 22.1% (*Picea ajanensis*), contained from 65.5% (oak) to 86.5% (*Picea ajanensis*) pure lignin. The rest consisted of carbohydrates.

3. Treatment of the lignin-carbohydrate complex ("crude" lignin) with hot water removed from 66.7 to 93.6% of the carbohydrates present. After this treatment, the dioxane lignin from the above-named species contained from 1.3 to 18.1% carbohydrates, on the weight of the lignin. The composition of this dioxane lignin was very close to that of lignin obtained by the use of concentrated acids.

4. The dioxane lignin is aromatic in character, but when it was oxidized by alkaline nitrobenzene the aldehyde yield was 1/2 to 1/5 of the yield obtained by direct oxidation of wood. This shows that oxidation in alkaline solution is too harsh for the soluble lignin isolated by such a mild method.

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INVESTIGATION OF THE NATURE OF HYDROLYTIC LIGNIN

A. P. Krasnov, S. I. Sukhanovskii, and M. I. Chudakov

About 200,000 tons of hydrolytic lignin, for which no significant uses have yet been found, is produced annually in the Soviet Union. Study of its chemical nature is therefore a task of great importance to the national economy.

The native lignin in wood undergoes irreversible processes of polymerization and condensation during hydrolysis, and is thereby converted into a complex aggregate of aromatic and carbohydrate residues, which are probably linked by carbon-carbon or ether linkages.

Investigation of the chemical nature of technical hydrolytic lignin is a complex problem, as the hydrolysis of wood itself depends on a number of factors difficult to take into account, so that it is not possible to obtain a standard reaction product of definite physicochemical properties. It is therefore difficult to reproduce the results obtained in investigations, and one can only speak of average values of particular characteristics in relation to technical hydrolytic lignin.

A method of alkali activation of hydrolytic lignin has been studied in considerable detail [1]; the alkali lignin so produced can be used for reinforcement of synthetic rubber in the latex stage.

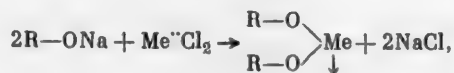
Alkali activation of hydrolytic lignin leads to the formation of a complex polydisperse system of the decomposition products of the lignin complex, formed as the result of parallel reactions of oxidation and demethylation.

Some of these products are of low molecular weight, readily soluble, and consist of acid substances which bind a considerable amount of the caustic soda used for the alkali activation.

The greater part of the lignin forms the so-called "lignin acids," which separate out on acidification of the alkaline solutions, in the form of amorphous flocculent precipitates with an enormous adsorption surface, effective in rubber reinforcement.

There is now no doubt concerning the phenolic nature of the hydroxyls in "lignin acids." This is proved by the formation of acetyl derivatives, good solubility in alkalies, liberation of the acids by the action of carbon dioxide, etc. However, the chemical nature of "lignin acids" is not yet understood.

The salts of "lignin acids" and univalent metals have relatively good solubility in water. Such solutions undergo exchange reactions with solutions of other salts, containing bi- or trivalent cations, with formation of insoluble salts of the "lignin acids" and multivalent cations:



where R is the "lignin acid" radical.

We attempted to determine whether these exchange reactions conform to any stoichiometric ratios, or whether the interaction is of a colloidal nature, caused by the coagulating action of the added electrolyte.

Lignin from the Leningrad hydrolysis plant, ground in a vibratory mill, was used in the investigation. The lignin contained 9.3% methoxyl groups and 2.8% ash. After treatment with alcoholic benzene and removal of residual polysaccharides, the methoxyl content rose to 10.3%. The lignin was treated with alkali at 180° for 4 hours. The alkali consumption for activation was 25% (on the lignin), and the liquor ratio was 7.5.

The solutions of sodium salts of "lignin acids" (alkali lignin) had 0.2-0.3% residual alkalinity. To eliminate excess alkali, the solutions were acidified to pH 6.5 and then centrifuged (at 3500 r.p.m.).

After separation of insoluble particles, the neutral solution of the sodium salts of "lignin acids" was used for exchange reactions with the following salts: BaCl₂, CuSO₄, CoSO₄, FeSO₄, NiSO₄, MnSO₄, CaCl₂, MgCl₂.

The amounts of salt solutions added were sufficient to ensure complete precipitation and the formation of almost colorless filtrates after separation of the precipitates by filtration.

The mixtures were heated on a water bath for 30 minutes to improve coagulation. The precipitates were then filtered off on porcelain funnels and washed to remove traces of soluble salts. It must be noted that this washing required 5-6 days with certain salts (Ni, Fe, Mg).

The dried precipitates were ashed. The percentage of metal in the original "lignin acid" salt and the amount of metal (in g-equiv.) per 1000 g of organic matter in the "lignin acids" were calculated in each case.

The results are given in Table 1.

TABLE 1
Experimental Results

Salts of	Ash %	Metal %	Amount of metal (in g-equiv.) per 1000 g of "lignin acids"
Barium	19.5	17.5	3.09
Copper	9.7	7.75	2.64
Cobalt	7.95	6.25	2.27
Iron	9.8	6.9	2.64
Nickel	8.5	6.67	2.44
Manganese	8.76	6.3	2.46
Calcium	8.18	5.86	3.10
Magnesium	6.41	3.87	3.3
		Mean	2.75

It follows from the data in Table 1 that 1000 g of "lignin acids" obtained by alkali treatment require about 3 g-equiv. of metal for salt formation.

It is seen that the reactions between the sodium salt of "lignin salts" and inorganic salts are exchange reactions which, in general, conform to stoichiometric proportions.

About 3 g-equiv. of alkali, or 120 g of caustic soda, is required to dissolve 1000 g of "lignin acids" (or "alkali lignin").

Since the expenditure of alkali in the alkali activation of hydrolytic lignin is in the range of 200-250 g per 1000 g of the starting material, it follows that over 50% of the caustic soda is expended in binding the acid products formed in the decomposition of the lignin complex [2].

The behavior of the "lignin acids," their chemical properties, solubility in alkalis, and the presence of phenolic hydroxyls and possibly of carboxyls in the molecule — all these facts indicate that there is an essential difference between them and the original hydrolytic lignin.

It is known [3-5] that the presence of aromatic groups in hydrolytic lignin is proved by the method of alkaline fusion, which gives, in 5-10% yield, a mixture of protocatechuic acid and pyrocatechol.

We proposed a method [6] for alkaline thermolysis of lignin in an inert heat-transfer medium (petrolatum), which also results in formation of protocatechuic acid, in similar yields.

It was of interest to compare the yields of aromatic substances from hydrolytic lignin and from "lignin acids" obtained from the same samples of hydrolytic lignin after alkali activation in caustic soda solution at 180°. Weighed samples of absolutely dry hydrolytic lignin and of the corresponding "lignin acids" were mixed with caustic soda and calcium oxide, the iron salts of "lignin acids" being added as catalyst.

TABLE 2
Yields of "Crude Protocatechuic Acid"

Proportions of components	Yield (%)
Hydrolytic lignin : caustic soda : calcium oxide = 1 : 1 : 1	6.32
Ditto, with "lignin acids" from the original hydrolytic lignin	1.32
Hydrolytic lignin free from polysaccharides and resins : caustic soda : calcium oxide : iron salt of "lignin acid" = 1 : 1 : 1 : 0.25	8.7
Ditto, with "lignin acids"	3.6

After thorough mixing, granulation, and drying, each sample was put into a wire beaker and placed in molten petrolatum at 270°. After exposure at this temperature for 1.5 hours the granules were washed free of petrolatum by boiling in benzene, dried, dissolved in water, and the solution was immediately acidified with 20% hydrochloric acid. The brown amorphous precipitate was filtered off and washed with water. Oxalic acid was not detected in the filtrate. Aromatic substances were extracted from the filtrate in ether, dried for a long time over caustic soda in a vacuum desiccator, and weighed.

The reddish oily liquids so obtained usually crystallized, and gave all the characteristic reactions of protocatechuic acid. After purification with animal charcoal and recrystallization from water, the products melted at 190-194°.

The yields of the unpurified product, provisionally described as "crude protocatechuic acid," are given in Table 2.

It follows from the data in Table 2 that the yields of aromatic substances from "lignin acids" are considerably lower than from the original lignin. The possible explanation is that alkali activation results in the removal of a large proportion of the aromatic protocatechuic groups, which are broken down at the high temperature and high pH.

Nikitin [7] suggested that lignin is split into fragments of low molecular weight by "chipping" of individual, less-firmly-bound groups from the main lignin skeleton.

To determine the changes which occur in hydrolytic lignin during the consecutive reactions on alkaline thermolysis, it was subjected to "chipping" by the action of heat at various temperatures in petrolatum.

The hydrolytic lignin was deresinified and freed from polysaccharides. The washed and dried product was subjected to three consecutive treatments in a mixture with caustic soda and calcium oxide. The components were in the following proportions in all cases: lignin : caustic soda : calcium oxide = 1 : 1 : 1. The fusion was performed in petrolatum at 180, 200, and 270°. After each fusion the "lignin acids" were isolated, analyzed, and subjected to further alkaline thermolysis.

The oxalic and protocatechuic acid yields were determined in the filtrate after isolation of the "lignin acids." The original hydrolytic lignin was treated in the first fusion, and the "lignin acids" formed were treated in the subsequent fusions.

The results are summarized in Table 3.

TABLE 3

Results of Experiments on the "Chipping" of Hydrolytic Lignin by the Action of Heat

Product	Yield, % on the original hydroly- tic lignin	Yield, % on the preced- ing lig- nin acids	Ash content, (%)	Analytical data (%)			Contents in filtrate (%)	
				OCH ₃	C	H	proto- cate- chuic	oxalic acid
Hydrolytic lignin	—	—	2.46	10.3	63.13	5.11	—	—
"Lignin acids" after thermolysis at 180° (A)	62.4	—	0.61	9.3	64.29	4.99	Nil	3.52
"Lignin acids" after thermolysis of (A), pre- ceding "lignin acids," at 200° (B)	50.0	80.0	0.50	8.53	65.13	4.87	Nil	Nil
"Lignin acids" after thermolysis of (B), pre- ceding "lignin acids," at 270° (C)	29.2	68.0	0.60	3.52	65.62	4.78	Traces	Nil

These results confirm the labile nature of the aromatic (protocatechuic) group in hydrolytic lignin; this group disappears almost entirely if the original material is subjected to repeated alkali treatment. The results also show that the "lignin acids" obtained from hydrolytic lignin do not yield aromatic substances (protocatechuic acid or pyrocatechol) in subsequent fusions, but are split into low-molecular oxidation products.

Our results do not confirm Hägglund's views [8]; he regarded "lignin acids" as intermediate products between lignin and aromatic decomposition products. Neither do they confirm the views of Heuser and Herrmann [4], who considered that "lignin acids," which are very resistant to oxidative breakdown, may be subjected to additional fusion to yield aromatic substances.

"Lignin acids," formed from hydrolytic lignin either by alkali activation in solution, or by alkaline fusion, do not give any appreciable yields of aromatic substances after additional alkaline thermolysis.

Consecutive treatments of "lignin acids" result (as follows from Table 3) in a decrease of the methoxyl content from 10.3 to 3.52%, and a change of the elementary composition; the percentage content of hydrogen decreases (from 5.11 to 4.78%), and the carbon content increases (from 63.13 to 65.62%).

It must be pointed out that the lignin nucleus, which is the most resistant, has a low methoxyl content (3.52%), although its oxygen content is approximately the same as that of the original hydrolytic lignin.

The relatively easy removal of the protocatechuic group from hydrolytic lignin (nearly 80% is split off during alkali activation in solution at 180°) shows that this group is probably linked by an ether bond to the main heterocyclic lignin complex.

SUMMARY

1. It was shown in a study of the behavior of the sodium salt of "lignin acids" in exchange reactions with solutions of divalent metal salts that these reactions are, in general, stoichiometric, 3 g-equiv. of metal being consumed per 1000 g of "lignin acids."
2. The "lignin acids" formed by alkali activation of hydrolytic lignin are considerably poorer in aromatic protocatechuic groups, of which 8-10% is present in the original hydrolytic lignin.
3. Repeated alkaline thermolysis of "lignin acids" does not give an additional yield of protocatechuic acid, but leads to demethylation, increase of the carbon content of the residue, and oxidative decomposition of the organic lignin substance.

4. It is suggested that the protocatecholic group is linked by an ether bond to the main heterocyclic complex of hydrolytic lignin.

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LOW-SUBSTITUTED Na-CARBOXYMETHYLCELLULOSE AND ITS PROPERTIES AS A FINISH FOR TEXTILES

G. A. Petropavlovskii and G. G. Vasilyeva

A number of the properties of cellulose, such as hygroscopicity, solubility, and reactivity, depend on the intermolecular forces, degree of orientation and the arrangement of the macromolecules in the fiber. Interaction between active hydroxyl groups of neighboring macromolecules in the fiber, effected mainly by hydrogen bonding, can be weakened by the introduction of a small number of bulky radicals into the cellulose [1].

Therefore slight etherification of cellulose fibers results in the formation of considerably more hydrophilic products. The lyophilic properties of cellulose can also be considerably improved by certain other treatments. Increase of the swelling of cellulose, and especially of its low-substituted ethers, in alkaline solutions at low temperatures and after freezing is of practical interest. It has been shown [2] that this method can be used to effect complete solution of certain low-substituted cellulose ethers of a high degree of polymerization.

For example, it is possible to obtain alkaline solutions of carboxymethylcellulose (CMC) of very low degrees of substitution in this way. Since the consumption of reagents is much less in the production of low-substituted cellulose ethers, their production and purification are simpler than in the case of products of a high degree of substitution.

We therefore studied certain properties of low-substituted Na-carboxymethylcellulose and its solutions, in relation to their possible use in the textile industry.

More than 35,000 tons of starch and flour are used annually in the textile industry for warp sizing in weaving, for finishing, and for thickeners in printing [3]. This raises the necessity of finding effective substitutes for these food products. Moreover, ordinary starch and paste finishes are washed off completely during the first launderings, and therefore cannot have a significant influence on wear resistance of the fabrics; laundering also destroys the finishing effect. It is therefore also important to find finishes which would not only act as temporary finishes for cotton fabrics, but would raise their abrasion resistance, which is the main factor in the wear resistance of fabrics. Alkali-soluble cellulose ethers [4], pectin and hide glues [5], chitosan [6] and other substances have been used as substitutes for starch and flour. With the development of carboxymethylcellulose production,* this substance is now being used in the textile industry for yarn sizing, as a pigment thickener, and for fabric finishing [7-12].

However, at present only water-soluble preparations of a relatively high degree of substitution (γ about 80) are mainly used. If the freezing method is used for dissolving, it is possible to obtain carboxymethylcellulose which is insoluble in water and dilute caustic soda at ordinary temperatures, but is readily soluble in dilute alkali at low temperatures. If this carboxymethylcellulose is deposited on fabrics from solution, it forms a finish which is fairly resistant to washing at normal or elevated temperatures, both in neutral and in weakly alkaline media.

An account is given below of some of our experiments on the production of solutions of low-substituted carboxymethylcellulose, suitable for textile finishing. The first investigations dealt with the possibility of increasing the CMC concentration in solution, and with the most economic decrease of the alkali concentration.

Low-substituted Na-carboxymethylcellulose was prepared by treatment of bleached sulfite wood pulp with aqueous alkaline solution of monochloroacetic acid with 17% free alkali.

*Over 35,000 tons annually.

The reaction was continued for 4 hours at 40°; at the end of this time the CMC was pressed out to 2.6-2.8 weight ratio, shredded, and aged. At the end of a definite aging period the Na-CMC was washed with distilled water on the filter to a neutral reaction, and dried in air.

The degree of substitution, fractions soluble in 6.5% NaOH (at room temperature and after freezing), and average degree of polymerization of the products were determined.

The results of these experiments, with comparative data on CMC obtained under the same conditions but without aging, are given in Table 1.

TABLE 1

Results of Experiments on Preparation of CMC

Consumption of CH_2ClCOOH (moles/mole of cellulose)	Moisture content of air-dry CMC (%)	Degree of sub- stitution γ	Solubility in 6.5% NaOH (%)		Average degree of polymeri- zation	Aging time at 20° (hours)
			at room tempera- ture	after freezing		
0.4	10.4	4.9	30.93	100	229	48
0.4	—	5.0	24.8	98.0	940	—
0.8	12.45	11.2	80	100	585	24
0.8	—	9.4	63.5	100	940	—
1.0	14.0	22.0	92.5	100	738	18
1.0	—	16.95	85.5	100	930	—

It follows from the data in Table 1 that the solubility of low-substituted carboxymethylcelluloses at low temperatures in 6.5% NaOH remains almost constant with decrease of degree of polymerization, and is almost complete even at low values of γ , attained with a small consumption of monochloroacetic acid. With small amounts of monochloroacetic acid, the degree of substitution did not increase after aging. With larger amounts of monochloroacetic acid there is an appreciable increase of the degree of substitution after aging.

Therefore, in the preparation of low-substituted Na-carboxymethylcelluloses, aging of the product after etherification serves only to lower the solution viscosity and therefore to increase the concentration of carboxymethylcellulose in solution. We succeeded in preparing solutions containing up to 6-8% CMC in 6.5% NaOH from low-substituted CMC made by this method.

To determine the possibility of a further decrease in the consumption of alkali, the stability of solutions of low-substituted carboxymethylcellulose after dilution was investigated.

Solutions of CMC in 4 and 6% caustic soda, prepared by the freezing method, were diluted severalfold with distilled water; the minimum alkali concentration at which turbidity or precipitation occurred was noted.

The results of these experiments are given in Table 2. They show that solutions of low-substituted Na-carboxymethylcellulose are fairly stable even when diluted to very low alkali concentrations, down to 0.5%.

This fact is very important in relation to the preparation of Na-carboxymethylcellulose solutions for practical purposes.

Solutions of low-substituted Na-CMC in 6.5% alkali, made by the freezing method, were next tested as fabric finishes. The finishing was performed as follows: the fabric (A 108 calico, 5.7% moisture) was placed in the solution of low-substituted carboxymethylcellulose for 3 minutes and then squeezed out between rollers. The squeezed-out piece of fabric was transferred to a precipitating bath containing 10% ammonium sulfate or 1 N H_2SO_4 . After 15 minutes in the bath, the specimen was washed thoroughly in distilled water. The fabric was stretched in the wet state over a wooden frame and dried at 100-105° to constant weight. The amount of finish was then determined in the dry finished piece.

TABLE 2

Stability of Na-CMC Solutions on Dilution

Exper. No.	γ of CMC	CMC concentration (%)	NaOH concentration (%) *	Visual observations on dilution
1	20.2	2.0	5.93	Original solution
2		1.0	3.0	} No change
3		0.67	2.0	
4		0.50	1.5	
5		0.40	1.2	} Faint opalescence after 24 hours
6		0.33	1.0	
7	20.2	2.0	4.17	Original solution
8		1.0	2.0	} No change
9		0.67	1.3	
10		0.50	1.0	
11		0.40	0.8	} Faint opalescence after 1 hour
12		0.33	0.66	
13	11.2	4.0	6.5	Ditto, and precipitate after 24 hours
14		2.0	3.2	Original solution
15		1.3	2.1	} No change
16		1.0	1.6	
17		0.8	1.3	
18		0.66	1.08	} Faint opalescence after 0.5 hour
19	22.0	5.0	6.5	Original solution
20		2.5	3.2	} No change
21		1.67	2.1	
22		1.25	1.6	
23		1.0	1.3	} Opalescence after 30 minutes
24		0.83	1.08	
25		0.71	0.93	
26		0.50	0.65	} Opalescence immediately on dilution
27		0.41	0.53	

* The solutions used in Experiments 2-6, 8-12, 14-18, 20-27 were obtained by 2,3,4-fold, etc., dilution of the original solutions.

The results showed that the amount of finish in the fabric depends mainly on the viscosity of the Na-CMC solution, i.e., on its concentration (for a given degree of polymerization).

The results of these experiments are given in Table 3.

It follows from the data in Table 3 that the amount of finish on the fabric increases in proportion to the CMC concentration.

Favorable results were also obtained by the use of Na-CMC solutions made by dilution, for fabric finishing.

The amount of finish in the fabric is greater in such cases than when an undiluted solution of Na-CMC in 6.5% alkali is used for finishing (with the same CMC concentration).

The explanation for this is probably that the fabric is impregnated better by dilute solutions. Therefore diluted solutions of CMC of low alkalinity can be used for fabric finishing. This is very important under production conditions, as the consumption of alkali in preparation of the finish liquor is reduced, with a corresponding reduction of the cost of the finish itself.

Another method of reducing the consumption of alkali in the preparation of finish liquors is to prepare these liquors by the freezing of the reaction mixture with a small addition of alkali immediately after etherification, without isolation of the CMC. In our experiments the solutions were prepared as follows: the cellulose was etherified by the method described earlier. At the end of the etherification (4 hours at 40°) the

calculated amount of NaOH was introduced into the reaction flask, to make the alkali concentration 6.5%, and the CMC concentration 1%. The mixture was frozen by the usual method, and the solution after thawing was used for finishing.

TABLE 3

Effect of Concentration of Na-CMC Solution on the Amount of Finish in the Fabric

η CMC = 11.2; NaOH concentration = 6.5%; DP = 585

Concentration of CMC solution (%)	Specific viscosity	Amount of finish (as % of the original material) applied in precipitating bath	
		in 10% ammonium sulfate solu.	in 1 N sulfuric acid
0.25	0.9	0.42	0.36
0.50	2.54	0.57	0.72
1.0	9.8	1.47	1.59
2.0	36.2	3.59	3.99
3.0	95.0	5.7	—
5.0	—	10.35	—

The amount of finish applied to the fabric was the same as in the use of solutions of purified Na-CMC.

The finish liquor made by freezing without isolation of CMC is yellow, probably owing to the color of cellulose degradation products, oxycelluloses. However, this color does not effect the fabric, as these products are soluble and are easily washed out when the finished fabric is rinsed in water.

Therefore CMC solutions prepared from CMC without isolation from the reaction mixture are also quite suitable for fabric finishing.

The laundering resistance of the finishes on the fabric was studied next.

A soap solution, containing 5 g of 60% oleate soap and 3 g of soda ash in 1 liter of distilled water, was prepared. The specimen was completely immersed in the soap solution at 40° for 30 minutes. The ratio of the volume of solution (in ml) to the weight of the specimen (in g) was 50:1.

After 30 minutes the specimen was taken out, squeezed, and returned to the solution. The immersion and squeezing were repeated 10 times, and the specimen was then rinsed in distilled water. The rinsing was carried out first with warm water (40-50°), and then with cold. The rinsed fabric specimen was dried in a drying oven at 105° to constant weight, and the amount of finish removed by the laundering was determined. The stability of the finish to soap solution at 100° was determined separately.

TABLE 4

Laundering Resistance of the Finish

Wash No	Concentration CMC solution (%)	Degree of polymerization of CMC in solution	Amount of finish removed during laundering (% of initial amount) at washing temp. (°C)	
			40	100
1	} 0.5	738	9.7	18.5
2			0.0	4.4
3			0.0	1.05
Total in three washes			9.7	23.95

TABLE 5

Effect of Degree of Polymerization of CMC on the Loss of Finish in Laundering

Degree of polymerization	Number of washes	Losses of finish in 3 washes at 40° (% of initial amount)
738	3	7.24
1540	3	3.44

Table 4 shows the laundering resistance of low-substituted carboxymethylcellulose finish at 40 and 100°.

It follows from Table 4 that the CMC finish is fairly stable, as only 9 to 23% of the initial amount present in the fabric is lost in three washes. More finish is lost at 100° than at 40°. The laundering losses can be reduced by the use of CMC with a lower degree of substitution and a higher degree of polymerization.

TABLE 6

Effect of Degree of Substitution of CMC on the Loss of Finish in Laundering

γ	Number of washes	Washing temp. (°C)	Losses of finish in 3 washes (% of initial amount)
11.2 22.0	3	100	15.17
			23.19

The results of our experiments on the stability of finishes based on CMC with different degrees of polymerization and γ are given in Tables 5 and 6.

Table 5 shows that the laundering resistance of the finishes increases considerably with increasing degree of polymerization of the CMC.

It follows from the data in Table 6 that the laundering resistance of the finishes decreases with increasing degree of substitution of the CMC. The reason is that more highly substituted CMC is more hydrophilic.

The strength of the finished fabric is of great importance in relation to the properties of the finish. Preliminary experiments were carried out to determine the tensile strengths of the finished fabrics. The results

showed that at low concentrations of Na-CMC in the finish liquors the fabric strength remains almost unchanged. With increase of the concentration of CMC in the solution to 4%, the tensile strength of the fabric increases by 12-15%.

SUMMARY

1. If alkaline carboxymethylcellulose is aged after etherification, the solution viscosity is decreased considerably, so that the concentration can be raised to 6-8%.
2. Low-substituted carboxymethylcellulose is not precipitated from solutions in 6.5% NaOH when diluted down to 0.5% alkali concentration.
3. Solutions of low-substituted Na-carboxymethylcellulose in alkali are suitable for fabric finishing. The amount of finish applied to the fabric increases with the concentration of the carboxymethylcellulose solution.
4. Carboxymethylcellulose finishes are fairly resistant to washing (the loss in 3 washes is 15-20%), and are much better than starch in this respect.
5. The stability of carboxymethylcellulose finishes to washing increases with increasing degree of polymerization, with increasing concentration in the finish liquor, and with decreasing degree of substitution γ .
6. Preliminary determinations of the tensile strength of finished fabrics showed that at low concentrations of carboxymethylcellulose the fabric strength is almost unchanged. At higher concentrations of carboxymethylcellulose the finished fabric is stronger than the original.

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SUBSTITUTE FOR CRUDE PINE TAR IN RUBBER RECLAIMING

A. A. Liverovskii, E. I. Shmulevskaja, and S. A. Sokolov

The utilization of scrap rubber in the form of good-quality reclaim is an important economic task.

The principal reclaiming process in present use is the aqueous neutral process, based on the heat treatment of the shredded rubber, mixed with softeners, in an aqueous medium. Pine tars occupy a special position among the softeners in the amounts used and in their influence on the quality of the product.

Qualities Required in Tars Used for Reclaiming

Pine tars occupy a leading place among the softeners now in use, as they conform to a number of requirements of the reclaiming industry. A good softener should swell the rubber. As it remains in the mass and acts as a plasticizer, it must not contain substances which cause aging of the reclaim and lower the physical and mechanical properties of the product. Its boiling range should be high.

The favorable action of pine tars in reclaiming is due to the specific effects of their constituents; of these, the following influence the quality of the reclaim.

Water-soluble substances. Pine tars contain up to 10% of water-soluble substances (fatty acids, alcohols, phenols, etc.). It has been found that removal of the water-soluble substances from pine tars alters their effect in reclaiming, the reclaim having higher plasticity (by 20-25%), and lower strength characteristics (by 20-30%).

The acidity of the softener mixtures should be about 2% (calculated as acetic acid), as with lower acidity the textile material in the scrap is not destroyed, while higher concentrations worsen the plastic properties of the reclaim.

Phenolic substances act as oxidation inhibitors and confer increased hardness on the reclaim; remaining in the final product, they increase its resistance to aging.

Resin acids are characteristic constituents of pine tars. By GOST No. 6288-52, pine tar for reclaiming is graded in three qualities according to the resin acid content; Grade I, not less than 30%, Grade II not less than 25%, and Grade III not less than 20%.

Resin acids favor the formation of a denser, tacky product with good physical and mechanical characteristics.

Substances insoluble in benzine.* The contents of benzine-insoluble substances in pine tars vary over a wide range, from 3 to 22%. This group consists of substances of different chemical nature; oxidation products of the resin acids and the products formed in secondary thermal reactions of the native resin acids are probably of interest in relation to reclaiming. The presence of these substances in the tar favors the formation of a reclaimed product with a clean and smooth surface, with increased strength, and readily worked in the finishing equipment.

Neutral oils. The use of neutral oils as softeners confers increased plasticity on the reclaim and lowers its strength.

Neutral pine-tar oils are superior to petroleum oils in reclaiming, but are inferior to the less saturated hydrocarbons in shale tar, coal tar, etc.

* As in original — Publisher's note.

Pine tars made in small plants, while being among the best softeners, have an important technological disadvantage: variable composition and hence variable technological properties. As the technological properties of pine tars depend on the proportions of the constituents present, it is possible to obtain a softener with constant technological properties by mixing tars with suitably selected analytical characteristics. For example, it is possible to improve the technological properties of a large supply of tars (from the Eastern, Western, and Central regions), which have low contents of substances insoluble in benzine, by the addition of a tar of analogous composition to pine tars but with a higher content of substances insoluble in benzine.

The use of SVTS tar, made by the Vakhtan* rosin works, for this purpose is considered in this paper.

Pine tars. The so-called pine tars are made by dry distillation of resinous wood in batch units heated by external combustion.

The quality or grade of pine tar depends on the material of the still (metal or brick), the system used for collecting the volatile products (overhead, bottom, or combined), and especially on the raw material.

From the historical standpoint, since these products were used for waterproofing impregnation (ropes, nets, hulls of wooden ships), their value was ultimately determined by the contents of resin acids and their thermal decomposition products.

Because of the low productivity of wood-distillation plants and the labor required for preparation of the resinous wood, the price of pine tar is high (2100 rubles per ton and over). As the equipment and technological processes used are not standardized, this tar is very variable and inconsistent in its physicochemical properties.

As the small undertakings are scattered all over the forest lands of the Union, and are at long distances from railroads, transport costs are high and the tar cannot be conveyed in tank cars.

Therefore the tar is transported in wooden barrels, often of inferior quality. The consumer must pay for the containers (500 rubles per ton), and loses much tar in the stores.

Because of all these facts, reclaiming plants are seeking to replace pine tars by new softeners, of lower cost, and constant physicochemical properties, which involve no inconvenience in transport and storage. In our opinion, the above-mentioned SVTS tar is such a material.

SVTS tar as a substitute for pine tars. SVTS tar is obtained by thermal decomposition of extracted resinified wood chips in the shaft of a gas producer of the Central Scientific Research Institute for Boilers and Turbines, designed by V. V. Pomerantsev and installed in the Vakhtan rosin-extraction plant.

This plant converts resinified tree stumps, extracting the resinous products in benzine, and produces rosin, turpentine, and flotation oil from the extracts.

The resin content of the original material is about 20%. After the extraction, the chips contain about 6% residual resins. These chips** were burned in boiler furnaces, without utilization of the wood chemicals.

When the producer was installed, it became possible to collect the chemical products formed by destructive distillation and at the same time to reach a high steam output in the boiler unit, so that the fuel was used both for power production and as a source of chemicals.

Because of the considerable content of residual resins in the fuel chips, a tar is obtained with a content of resin acids which approaches that of some grades of pine tars mentioned earlier. The tar was tested as a softener in rubber reclaiming. The first trials showed that it was suitable in principle for this purpose, but it was found that the content of water-soluble substances must be lowered. Moreover, one of the essential conditions for the use of the tar for this purpose was a constant content of resin acids.

To solve these problems, we devised a method for washing SVTS, which decreases the content of water-soluble substances and increases the relative content of resin products. By operation of this process on the technical scale it proved possible to produce SVTS of consistent quality. The wash liquor, containing carbohydrate materials, was recommended for use as a casting binder by the method of the Central Scientific Research Institute of the Wood Chemical Industry, developed for acid liquors from wood-fired gas producers.

* Transliteration of Russian — Publisher's note.

** To augment the fuel balance, some firewood is added to the chips, the amount varying according to the time of the year.

TABLE 1

Analyses of Tar Samples

Type of tar	Moisture (%)	Mechanical impurities (%)	Density d ₂₀	Contents (% on absolutely dry tar)							yield of oils on distillation	
				water-soluble acids	volatile acids	insoluble in benzene	phenols	nominal resin acids				
								total	including			
									fatty	unoxidized		oxidized
Dry-distilled birch wood tar	5—20	—	1.1 —1.07	3.5	2—4	20—25	12—25	6—7	36.00	Nil	45.00	40—70
Gas-producer Segezha tar	20—30	1.0—1.60	1.1 —1.20	—	—	38—42	10—12	15—25	36.5	38.20	6.5	40—70
Pine tars	2—8	0.2—0.5	1.05—1.13	1.0—2.5	—	5—20	5—10	15—42	10.01	59.75	28.12 *	30—40
SVTS tar	7—20	0.5—1.5	1.1 —1.28	1.5—5.1	1.0—3.0	50—60	5—10	10—25	23.7	53.5	14.5	20—30

*From ether extract.

The analytical data for the washed tar, obtained by a continuous process in the plant during the past two years, are fairly consistent.

Analyses of the tar during this period, carried out in accordance with the requirements of the reclaiming industry in relation to pine tars, gave results in the following ranges (%): moisture 10-20, substances insoluble in benzene 50-60, water-soluble acids 1.5-3.5, resin acids 15-22, water-soluble substances 5-10.

The resin acids were determined by extraction of the tar with benzene, the method generally used for pine tars, with subsequent treatment of the benzene solution to extract the resin acids. As stated above, the tar is found to contain 15-20% resin acids. In view of the fact that, in the primary treatment of the resinous chips with benzene to extract resins, in the principle process of the Vakhtan plant mainly unoxidized resin acids are extracted, it was presumed that SVTS tar should have a higher content of oxidized resin acids.

To confirm this, the tar was extracted with ether which dissolves oxidized resin acids to a considerable extent. The total yield of resin acids was about 30-35% on the absolutely dry tar. Separation of the isolated resin acids into fatty acids, unoxidized resin acids, and oxidized acids showed that the total contained about 19.55% fatty acids, 31.26% unoxidized acids, and 35.50% oxidized acids.

As stated earlier, the presence of oxidized resin acids in the tar confers a number of favorable properties to the reclaim, and their presence in the tar is desirable from this point of view.

Therefore, in determination of resin acids in benzene extract of SVTS tar a low result is obtained owing to the poor solubility of oxidized resin acids in benzene. It should also be noted that the resin acids isolated through their barium salts can only nominally be considered as resin acids. Barium salts precipitate certain hydroxy acids, which do not belong to the resin-acid class, and also a certain amount of phenols.

In the separation of nominal resin acids, the hydroxy acids and phenols remain with the oxidized acids.

Benzene extraction of tar is used if the tar is to be used in the fields of application of pine tars, with an established analytical procedure based on benzene extraction. For comparison of SVTS tar with other tars, the average data on its composition and analytical data on other tar samples are given in Table 1.

TABLE 2

Analytical Data on SVTS and Altai Tars

Contents (%)	SVTS	Altai tar
Moisture	8—19.8	4.8—6.0
Water-soluble acids	1.31—1.49	0.88—1.77
Insoluble in benzine	48.60	5.6
Resin acids from benzine extraction	16.5—21.9	24.30—38.0

The maximum contents of water-soluble acids and the minimum contents of resin acids are given for the unwashed tar in the data on SVTS tar.

The high content of resin acids in the tar from the Segezha hydrolysis plant is of interest. It is caused by the composition of the fuel (a high percentage of pine wood) and its quality (rather large and moist chips). Under these conditions a low yield of tar substances from the wood itself, and because of the relative ease with which natural resinous substances pass from the chips into the final tar, the latter has a high content of resinous substances. Therefore tar from the Segezha plant proved suitable in quality for use in the reclaiming industry.

Trials of the use of SVTS in the reclaiming industry. After favorable laboratory tests, SVTS tar was sent to the Chekhov reclaiming plant for tests in semi-industrial conditions. It was found that SVTS tar improves the technological properties of tars with low contents of substances insoluble in benzine. These results were used to improve the technological properties of pine tars from the Altai region, which are the main material used as softener in the Chkalovsk plant.

Average analytical data on a batch of SVTS and on Altai tar used in trials in the Chkalovsk plant are given in Table 2.

According to the plant reports, the trials showed that despite the low acidity of SVTS the amounts of textile material in the devulcanized product obtained with the use of a triple mixture are small, lower than with Altai tar.

No textile material was present in the devulcanized material obtained with a double mixture and with pure SVTS.

It was found under semi-industrial conditions that a firm and strong sheet of reclaimed rubber without tackiness is obtained with different amounts of SVTS and heavy oil. The reclaim had good physical and mechanical characteristics.

For example, with 30:15 ratio of SVTS to heavy oil, the tensile strength was 46 kg/cm², relative elongation 530%, softness 3.56 mm, elastic recovery 0.92 mm.

Production trials of SVTS were performed with triple tar mixtures. The results are given in Table 3.

The output of the refining equipment was 77-81 kg/hour for the experimental batches, refining losses 30-31%; for production batches without SVTS the output was 70 kg/hour, and losses in refining 33%.

As the result of extensive production trials of SVTS, it was concluded that the quality of the reclaim is improved by the use of SVTS in mixtures with pine tar and heavy oil.

Economic data. The use of SVTS tar in rubber reclaiming results in a considerable cost saving as compared with the use of ordinary pine tar.

The cost of SVTS tar is 550 rubles per ton; a ton of ordinary pine tar costs 2200 rubles. The saving is 1650 rubles per ton. The saving effected in 1954 by the use of 800 tons of SVTS tar in the plant was 1,320,000 rubles.

TABLE 3

Results of SVTS Trials with Triple Tars

Number of batches	Reclaim quality	Avg. temp. of trials (°C)	Tensile strength (kg/cm ²)	Relative elongation (%)	Softness (mm)	Elastic recovery (mm)	Notes
288	OS	31	48.4	540	3.15	0.66	Experimental batches of Altal tar and heavy oil 16:16:16 per 100 wt. parts of rubber
297	1	31	47.5	530	3.24	0.68	
288	OS	27	41.5	540	3.46	0.66	Production batches of Altal tar and heavy oil, 30:7.5 per 100 wt. parts of rubber
246	1	27	39.5	530	3.42	0.68	

According to the plant reports, the cost of raw materials with the use of triple mixtures containing SVTS is decreased by 14-17%, and with double mixtures (SVTS-heavy oil), by 25-33%.

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THE SYNTHESIS OF SOME ESTERS OF β -CHLOROPROPIONIC ACID

V. N. Mikhailova and V. V. Pigulevskii

The Leningrad Institute of Motion-Picture Engineers

Recently 1-phenyl-3-pyrazolidone, known under the name of phenidone, has come into use as a developer in photography [1, 2, 3].

One method for its synthesis is by the reaction of esters of β -halogenated propionic acids, including β -chloropropionic acid, with phenylhydrazine [4].

The object of the present investigation was the synthesis of certain esters of β -chloropropionic acid and a study of the simplest and most convenient methods for their preparation.

The methyl [5-8], ethyl [5, 6, 8, 9, 10], butyl [8], isobutyl [6], and isoamyl esters of β -chloropropionic acid, which have not been studied sufficiently, and also the isopropyl and octyl esters, which are not described in the literature, were synthesized and characterized (Table 1).

These esters may be prepared from acrylate esters or acrylonitrile.

The addition of hydrogen halides to acrylates was used for synthesis of these esters. Moureu, Murat, and Tanpier [8] carried out the reaction of hydrogen halide addition to acrylates in anhydrous ether solution on cooling.

It was found in the present investigation that hydrogen chloride is absorbed vigorously when passed through cold methyl acrylate (at 0°) in absence of solvent.

However, in this case only part of the hydrogen chloride is added at the double bond, while the rest remains in solution and is added only at a higher temperature. If the mixture is held at room temperature for at least 15 hours, the yield of methyl β -chloropropionate reaches 80-90% of the theoretical (Table 2).

Similar results were obtained by the addition of gaseous hydrogen chloride to acrylonitrile, which gives the nitrile of β -chloropropionic acid, yielding β -chloropropionic acid on saponification.

Stewart and Clark [12] saturated acrylonitrile with hydrogen chloride, with subsequent neutralization and distillation of the reaction product, without holding the reaction mixture after saturation.

It was found that when an equimolecular amount of hydrogen chloride is passed through cooled acrylonitrile (at 0°), the latter does not react completely, as part of it apparently remains in the dissolved state.

It was necessary to hold the reaction mixture at a higher temperature at the end of the reaction.

It was found that the nitrile of β -chloropropionic acid is obtained in 84-90% yield if an equimolecular mixture of hydrogen chloride and acrylonitrile is held at room temperature for more than 20 hours (Table 3).

Esterification of β -chloropropionic acid with certain aliphatic alcohols in presence of sulfuric acid, without separation of the water formed, gives the corresponding esters in 60-65% yield (Table 4).

Esters of β -chloropropionic acid were then synthesized directly from its nitrile, by the reaction



where R = CH₃, C₂H₅.

TABLE 1

Properties of Esters of β -Chloropropionic Acid

Formula of ester	Boiling point (°C, at pressure in mm)	Density d_4^{20}	Refractive Index n_D^{20}	Molecular refraction M_R		Chlorine content (molar %)		Literature data		
				found	calculated	found	calcd.	boiling point (°C)	density d	refractive index
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_3$	155—157 (760)	1.1583	1.4268	27.15	27.19	28.81	29.00	148—157	$d_4^{15} = 1.1861$	—
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OC}_2\text{H}_5$	162—163 (760)	1.0858	1.4264	32.14	31.81	—	—	161.4—161.8 (758 mm)	$d_4^{20} = 1.086$	$n_D^{20} = 1.4253$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OC}_3\text{H}_7$ (iso)	58—60 (3—4)	1.0820	1.4272	35.63	36.43	24.10	23.58	—	—	—
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OC}_4\text{H}_9$	9798 (8)	1.0868	1.4310	41.07	41.05	21.68	21.58	180	$d_4^0 = 1.0728$	$n_D^0 = 1.4389$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OC}_6\text{H}_5$ (iso)	189—190 (760)	1.0270	1.4280	41.21	41.05	21.43	21.58	191—193	$d_4^0 = 1.066$	—
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OC}_8\text{H}_{11}$ (iso)	100—102 (7)	1.0140	1.4320	45.66	45.66	19.75	19.85	207—208 (740 mm)	$d_4'' = 1.0443$	$n_D'' = 1.4380$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OC}_8\text{H}_{17}$	180—132 (4)	0.9758	1.4430	59.91	59.52	16.20	16.10	—	—	—

TABLE 2

Addition of Gaseous Hydrogen Chloride to Methyl Acrylate. Molar ratio $\text{CH}_2 = \text{CH}-\text{COOCH}_3$: $\text{HCl} = 1:1$, saturation time with hydrogen chloride 1 hour

Taken (g)		Time held at room temperature (hours)	Yield of $\text{CH}_2\text{ClCH}_2\text{COOCH}_3$	
$\text{CH}_2=\text{CH}-\text{C}(=\text{O})\text{OCH}_3$	HCl		g	%
36.9	15.9	2.0	32.9	62.5
54.5	23.2	2.0	47.9	61.5
37.8	16.0	15.0	43.3	80.5
65.5	27.8	48.0	82.4	88.5
29.2	12.5	48.0	37.3	89.6

TABLE 3

Addition of Gaseous Hydrogen Chloride to Acrylonitrile. Molar ratio $\text{CH}_2 = \text{CH}-\text{CN}$: $\text{HCl} = 1:1$, saturation time with hydrogen chloride 1.5-2 hours

Taken (g)		Time held at room temperature (hours)	Yield of $\text{CH}_2\text{Cl}-\text{CH}_2-\text{CN}$	
$\text{CH}_2=\text{CH}-\text{CN}$	HCl		g	%
8.48	5.85	0	4.85 *	33.9
14.60	10.07	10.0	17.00 *	69.1
6.84	4.73	24.0	9.00 *	77.9
20.46	14.08	0.5	17.05	49.3
23.06	15.90	2.0	20.30	52.1
6.68	4.60	15.0	8.20	72.7
24.54	16.90	24.0	34.60	83.5
12.24	8.43	48.0	18.15	87.8
7.68	5.3	48.0	11.75	90.6

* The reaction product was washed with soda solution.

TABLE 4

Esterification of β -Chloropropionic Acid. 2 ml of sulfuric acid ($d_4^{20} = 1.83$) used

Taken			Reaction time (hours)	Yield of ester	
β -chloro- propionic acid (g)	alcohols			g	in %
	formula	g			
8.95	CH ₃ OH	49.0	2.5	7.9	64.5
22.1	iso-C ₃ H ₇ OH	98.0	3.5	19.0	62.0
24.0	C ₄ H ₉ OH	98.0	5.0	23.5	64.5
5.0	iso-C ₄ H ₉ OH	98.0	5.0	4.7	62.0
26.0	iso-C ₅ H ₁₁ OH	98.0	6.0	27.0	63.0
25.0	C ₈ H ₁₇ OH	74.0	8.0	26.0	58.0

It was found that if the nitrile and water are present in equimolecular proportions in the system the ester is formed only in presence of considerable excess of sulfuric acid. If not enough sulfuric acid is present the reaction is confined to partial saponification of the nitrile. The addition of a considerable excess of water in the form of 93% sulfuric acid has no adverse effect on ester formation, the yields reaching 60% of the theoretical (Table 5).

TABLE 5

Synthesis of Methyl and Ethyl β -Chloropropionates from the Acid Nitrile

Composition of the reaction mixture (g),						Yields					
CH ₂ ClCH ₂ CN	CH ₃ OH	C ₂ H ₅ OH	100% H ₂ SO ₄	H ₂ O	H ₂ O : CH ₂ ClCH ₂ CN (moles)	unreacted CH ₂ ClCH ₂ CN		CH ₂ ClCH ₂ COOH		ester	
						g	%	g	%	g	%
10	29	—	0.42	2.12	1 : 1	6.0	60.0	4.0	35.0	0	0
10	29	—	27.8	2.12	1 : 1	—	—	0.8	6.15	5.3	36.0
16	115	—	108	9.00	3 : 1	—	—	—	—	14	60
16	—	115	108	9.00	3 : 1	—	—	—	—	16.0	60.5

The results of experiments on the esterification of β -chloropropionic acid with certain aliphatic alcohols are given in Table 4.

EXPERIMENTAL METHODS

Preparation of β -chloropropionitrile. Freshly distilled cold (0°) acrylonitrile was saturated with dry hydrogen chloride (1:1 molar). The reaction mixture was held at room temperature and distilled under reduced pressure. The β -chloropropionitrile boiled at 70-71° at 15 mm [12, 13].

It was found that neutralization of the reaction mixture by soda solution, as recommended by Stewart and Clark [12], is not necessary (Table 3).

Preparation of β -chloropropionic acid. β -Chloropropionitrile (38 g) was saponified by concentrated hydrochloric acid (37 g) by heating on a water bath for 3 hours [14]. The ammonium chloride which separated out was dissolved in water (30 ml). The reaction products were extracted in ether and dried with sodium sulfate. The solvent was distilled off to leave β -chloropropionic acid [15-21] in the form of white crystals with m. p. 39-40°, which agreed with literature data [15].

The total yield of the acid was 90% of the theoretical.

Synthesis of methyl β -chloropropionate from methyl acrylate. Freshly distilled cold (0°) methyl acrylate was saturated with dry hydrogen chloride in 1:1 molar ratio. The reaction mixture was held for different times at room temperature and then distilled through a fractionating column (Table 2).

The boiling point of the methyl β -chloropropionate after twofold distillation was 155-157°, in agreement with Henry's data [5].

Esterification of β -chloropropionic acid. The acid (m. p. 39-40°) was esterified by alcohol by the usual method, the mixture being heated in presence of concentrated sulfuric acid. The reaction product was extracted in ether, dried over sodium sulfate, and distilled through a fractionating column.

Synthesis of methyl and ethyl β -chloropropionates from β -chloropropionitrile. The calculated quantity of sulfuric acid was added dropwise with stirring to a mixture of nitrile and alcohol. The reaction mixture was heated for 7-8 hours on a boiling water bath.

The reaction product was neutralized, extracted in ether, and dried over sodium sulfate. After removal of the solvent, the ester was isolated by distillation through a fractionating column (Table 5).

SUMMARY

1. It is shown that when β -chloropropionitrile reacts with methyl or ethyl alcohol in presence of concentrated sulfuric acid, the corresponding esters of β -chloropropionic acid are formed.
2. The methyl, ethyl, isopropyl, butyl, isobutyl, isoamyl, and octyl esters of β -chloropropionic acid were prepared by different methods, of which the most promising are from the nitrile of the acid and the corresponding alcohol, and from the acrylates and hydrochloric acid.

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ALKYLATION OF ϵ -CAPROLACTAM AND ALIPHATIC DIAMINES BY CATALYTIC DEHYDRATION*

A. S. Shpital'nyi and I. V. Kuznetsova

The use of N,N'-dialkyl diamines has been proposed for the synthesis of modified polyamide resins, which form fibers of increased elasticity [1]. It has been shown [2] that N-methylcaprolactam can give rise to polyamide resins under certain conditions; therefore N-alkylated ϵ -caprolactam may also be used for this purpose. Therefore rational methods for the alkylation of these compounds are of great practical importance in addition to their theoretical interest.

The existing methods for the alkylation of ϵ -caprolactam and aliphatic diamines were primarily intended for laboratory preparations.

The alkylation of ϵ -caprolactam was described by Ruzicka [3] and by Benson [4]. Both used dialkyl sulfates as the alkylation agents. Ruzicka treated the sodium derivative of caprolactam with dialkyl (dimethyl) sulfate, whereas Benson alkylated ϵ -caprolactam in benzene solution, the dialkyl sulfate being added gradually to a solution of ϵ -caprolactam in benzene, heated on a water bath. Separation of the alkylated product from the reaction mixture involves some difficulties.

The following methods have been used for alkylation of diamines:

1) The Hofmann reaction [5].

2) Methods in which Schiff bases are formed as intermediate compounds: a) reducing alkylation, in which the already-formed Schiff base was reduced [6], or the formation and reduction of the Schiff base took place simultaneously [7]; b) alkylation by hydrolysis of the reaction products of Schiff bases with alkyl halides [8].

Other methods for the preparation of alkylated amines have been described, such as a method for preparing specifically secondary amines consisting of preparation of the monoacyl derivative of a primary amine, replacement of the remaining hydrogen at the nitrogen atom by metal, reaction of the resultant compound with an alkyl halide, and saponification of the acyl group [9], or by hydrogenation of a dinitrile in presence of a primary amine [10].

The published methods for alkylation of amines also include a method for preparation of N-alkylated derivatives of aromatic amines by means of catalytic dehydration [11]. The possibility of the use of this method for alkylation of aliphatic diamines or lactams is not considered in the communications dealing with this method.

The distinctive features of the alkylation of ϵ -caprolactam by catalytic dehydration are that the dehydration process itself is continuous, and that the separation of the pure product is relatively simple. A mixture of caprolactam and alcohol in the ratio of 3-5 moles of alcohol to 1 mole of lactam was continuously fed into an apparatus consisting of an evaporator, a reactor filled with catalyst, and a condenser connected to a receiver. The evaporator was maintained at 110-120°, and the reactor at 300-400°. The mixture was fed at a rate of 0.2 liter/hour per 1 kg of catalyst. Excess alcohol was distilled out of the distillate, and the alkylated product and unreacted caprolactam were then distilled off under reduced pressure. Methyl and ethyl alcohols were used as the alkylating agents. The catalyst was activated alum or activated alumina. Better results were obtained with alumina.

*Communication VI in the series on the formation of polyamide resins.

The influence of the reactor temperature on the yield of the alkylated product is illustrated by the data in Table 1.

TABLE 1

Influence of Reactor Temperature on the Yield of Alkylated ϵ -Caprolactam

Alkylating agent	Reactor temperature (°C)	Yield of alkylated product • (%)
Methyl alcohol	300	22.4
	350	88.0
Ethyl alcohol (96%)	300	8.9
	350	23.3

The alkylation of ethylene- and hexamethylenediamine was performed under the conditions described for ϵ -caprolactam. The best yields of the alkylated products were obtained with activated alumina catalyst, with the reactor at 350°. Analysis of the ethylation products of ethylenediamine and hexamethylenediamine showed that under the reaction conditions used, secondary amines were predominantly formed (Table 2).

EXPERIMENTAL METHODS

Preparation of N-methyl- ϵ -caprolactam. 110 g of a mixture consisting of 45 g caprolactam (0.398 mole) and 65 g methyl alcohol (2.03 moles) was heated in the preheater to 120° and passed through the reactor at 350° at 30 ml/hour. The reactor contained 150 g of catalyst. 100 g of distillate was obtained, from which 32.5 g of product was distilled at $p = 15\text{--}30$ mm and $t = 120\text{--}130^\circ$.

Found %: C 65.95; H 10.27; N 10.76, $n_D^{25} = 1.4825$ (according to Benson [4] $n = 1.4833$). $C_7H_{13}ON$.
Calculated %: C 66.13; H 10.23; N 11.02.

11.7 g of unreacted caprolactam was isolated.

TABLE 2

Results of Alkylation of Ethylenediamine and Hexamethylenediamine by Methyl and Ethyl Alcohols

Amine alkylated	Alkylating agent	Total amine nitrogen in distillate (g)	Amounts of nitrogen pertaining to amines (g)		Yield (%)		
			primary	tertiary	alkylated product	primary amines	secondary amines
Ethylenediamine	Methyl alcohol	10.854	4.837	0.1937	55.5	1.78	53.72
Hexamethylenediamine	Methyl alcohol	5.960	0.573	2.350	90.4	39.40	51.72
	Ethyl alcohol	6.160	1.410	1.620	72.3	26.30	46.00

Preparation of N-ethyl- ϵ -caprolactam. 103 g of a mixture consisting of 46.3 g caprolactam (0.409 mole) and 56.7 g of 96% ethyl alcohol (1.18 moles) was treated as described above. 84 g of distillate was obtained, from which 10 g of product with $n_D^{25} = 1.4790$ was distilled at $p = 5\text{--}10$ mm and $t = 95\text{--}110^\circ$. According to the literature, at $p = 5.5$ mm, $t = 97^\circ$, $n_D^{25} = 1.4777$.

12 g of unreacted caprolactam was isolated.

Methylation of ethylenediamine. 136 g of a mixture consisting of 65.7 g ethylenediamine (1.098 moles) and 70.3 g methyl alcohol (2.2 moles) was treated as described above. 121 g of distillate was obtained. Fractionation of the distillate yielded fractions containing 10.854 g of amino nitrogen. Analytical data on these fractions are given in Table 2. It is seen that the yield of the methylated product was 55.5%, and of secondary amines, 53.72%.

Methylation of hexamethylenediamine. 84 g of a mixture consisting of 40 g hexamethylenediamine (0.345 mole) and 44 g methyl alcohol (1.374 moles) was treated as described above.

The distillate (80 g) was heated on the water bath to remove the alcohol. The residue, 6.0 g, was fractionated. The fraction contained 5.96 g of amino nitrogen. The results of the subsequent analyses are given in Table 2, from which it follows that the yield of the methylated product was 90.4%, and of secondary amines, 51%.

Ethylation of hexamethylenediamine. 112 g of a mixture consisting of 51 g hexamethylenediamine (0.44 mole) and 61 g of 96% ethyl alcohol (1.27 moles) was treated as described above. The distillate (100 g) was heated on the water bath to remove the unreacted alcohol. The residue was analyzed, the results being given in Table 2. The yield of the alkylated product was 72.3%, and of secondary amines, 46%.

SUMMARY

It is shown that ϵ -caprolactam, ethylenediamine, and hexamethylenediamine can be alkylated by the catalytic-dehydration method.

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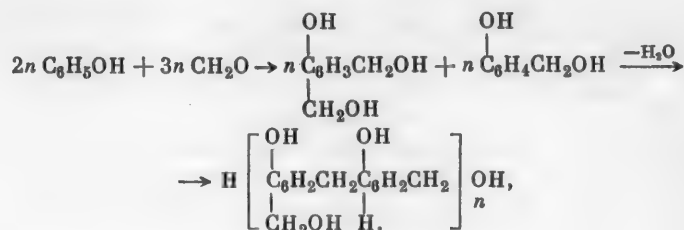
INVESTIGATION OF THE MECHANISM OF "HARDENING" OF PHENOL-FORMALDEHYDE RESOLES

A. A. Vansheidt and N. N. Kuznetsova

Institute of High-Molecular Compounds, Academy of Sciences USSR

The possibilities of technical utilization of soluble phenol-formaldehyde resins of the resole type depend mainly on the ability of these resins to "harden" and become infusible and insoluble resins of the resite type. Therefore the question of the hardening mechanism of resoles is of exceptional interest in relation to the theory and practice of phenol-aldehyde condensation. Nevertheless, this question cannot be regarded as completely solved as yet, although data are now available which give an indication of the chemical nature and structure of low-molecular products of phenol-aldehyde condensation.

It has been shown by Soviet workers [1-5] that phenol-formaldehyde resins of the novolac type are mixtures of polyphenols having the structure $H[C_6H_3(OH)CH_2]_n C_6H_4OH$, in the molecules of which $n + 1$ phenol residues are bound together at the aromatic nuclei by n -methylene groups, and that resole resins formed in an alkaline medium by polycondensation of the primary reaction products, i.e., mono- and dimethylol phenols, by a mechanism such as the following:



consist of mixtures of phenols, phenol alcohols, and polyphenols, containing unsubstituted H atoms as well as methylol groups in the ortho and para positions relative to the phenolic OH groups.

With regard to the hardening of resoles, it was formerly believed but not proved, that this process consists of further polycondensation of the resole molecules, between methylol groups of one molecule and unsubstituted H atoms of another, with formation of space polymers, containing trifunctional phenolic residues of the type

$HO - \text{C}_6\text{H}_2(\text{CH}_2\text{OH})_3$, linked in three dimensions in space by $-CH_2-$ groups. Therefore resites of the maximum degree of cross linking should have the composition $(HOC_6H_2)_2(CH_2)_3$, i.e., should contain 1.5 CH_2 groups for each aromatic nucleus; less cross-linked resites should contain less than 1.5 but more than 1 CH_2 group per nucleus, with all the phenolic hydroxyls remaining intact.

This theory was in good agreement with the insolubility and infusibility of resites, and also with the fact that they were formed only in the case of trifunctional phenols, containing 3 unsubstituted H atoms in the ortho and para positions.

However, recent experiments with so-called "model resoles," i.e., phenol alcohols without mobile H atoms in the aromatic nuclei, unexpectedly led German and Swedish workers [6] to a new concept, according to which the hardening of resoles is accompanied by formation of dimethylene ether bridges (from two methylol groups) and quinomethides (by intramolecular removal of water from phenolic and alcoholic hydroxyls), with subsequent conversion into di- and trimers.

Since, in contrast to model resoles, the phenolic nuclei of ordinary technical resoles always contain active H atoms, and alkaline or acid hardening catalysts assist the condensation of methylol groups at these H atoms, the claims of the foreign workers that such reactions may play a significant role in the hardening of ordinary resoles seemed to us very improbable.

For elucidation of the mechanism of formation and hardening of phenol-formaldehyde resins, and of the chemical nature of resites, we carried out a detailed chemical study of the transformations taking place on the heating of phenol alcohols and resoles formed from phenol and formaldehyde in presence of alkaline catalysts. We used a combined method, consisting of a quantitative investigation of the four consecutive transformations: $\text{phenol} + \text{CH}_2\text{O} \rightarrow \text{phenol alcohols} \rightarrow \text{resole} \rightarrow \text{resitol} \rightarrow \text{resite}$, with an exact balance of the reacting substances and the reaction products, and chemical analysis of the reaction products at all the conversion stages.

The volatile products liberated at each stage were completely collected and determined quantitatively, and the nonvolatile products were analyzed for contents of phenol, OH groups, carbon, and hydrogen. The free phenol in the resins and phenol alcohols was determined bromometrically after steam distillation, and directly in the volatile products, so that the amount of phenol combined at each stage could be determined.

The total OH-group contents, both of the phenol alcohols and soluble resins, and of the insoluble but swelling hardening products, were determined by acetylation in pyridine; the results were compared with the results of elementary analysis, so that it was possible to determine whether all the oxygen in the resins is present in the form of OH groups.

The alcoholic hydroxyls of the methyl groups were determined by the method of Vansheidt, Itenberg, and Shtraikhman [5], consisting of condensation of the phenol alcohols with a large excess of phenol in an acid medium, followed by quantitative determination of the unconsumed phenol.

The methylene groups binding the aromatic nuclei in the polycondensation products of phenol alcohols, i.e., in resoles, resitols, and resites, could not be determined directly owing to lack of chemical methods for their determination. However, their contents in the polycondensation products could be estimated by exact determination of the amount of water evolved during the condensation, if this water was evolved during the reaction only as the result of condensation of methylol groups of one molecule with aromatic nuclei of another (i.e., if one molecule was liberated per CH_2OH group), and not evolved by the interaction of pairs of methylol groups or of methylol groups with phenolic hydroxyls with formation of ether groups (i.e., with the disappearance of two hydroxyl groups for each molecule of water formed); this could be checked by analysis of the reaction products.

Formation of phenol alcohols. Phenol alcohols were prepared by a method similar to that described by Vansheidt and Vasil'ev [7], from a mixture of phenol and formaldehyde, containing 1 mole of formaldehyde and 0.036 mole of caustic soda per mole of phenol.

The table contains the result of two series of experiments, with the percentage compositions of the reaction mixtures before heating, and after heating until the disappearance of free formaldehyde in the formation of phenol alcohols. It follows from the data in the Table that in Experiments I and II 1.7-1.5 moles of formaldehyde were combined per mole of reacted phenol, and therefore a considerable proportion of the phenol (over 1/3) remained free.

The phenol alcohols obtained by the action of heat on phenol with formaldehyde contained more than 1/3 of water; they were therefore dried by distillation of the water under vacuum at 40°. Some of the phenol distilled with the water. The vapor from the flask passed through a condenser into a receiver cooled to -15° with a mixture of ice and salt, then to a coil contained in a Dewar flask with solid carbon dioxide, and into an absorption flask containing concentrated sulfuric acid.

Results of Experiments, Series I and II*

Contents (%)	Phenol alcohols		Resole		Resitol		Resite	
	I	II	I	II	I	II	I	II
Phenol free bound	28.3 45.5	24.6 49.8	7.5 72.6	6.9 73.9	0 83.4	1.4 83.4	0 86.0	0 86.6
Total	73.8	74.4	80.1	80.8	83.4	84.8	86.0	86.6
Formaldehyde free bound as CH ₂ OH	0 25.2	0 24.4	0 10.8	0 10.2	0 3.9	0 2.1	0 0	0 0
Distilled off phenol water	7.6 9.8	6.8 8.5	0.9 4.2	1.5 5.0	0 3.0	0 2.0	— —	— —
Total	17.4	16.3	5.1	6.6	3.0	2.0	—	—
Yield of resin, on the starting material	82.6	88.7	94.9	98.4	97.0	98.0	—	—
Total OH calculated by Formula 1	27.8	27.5	20.8	20.6	17.5	16.7	15.8	15.8
from the oxygen content	27.3	26.9	20.3	19.8	17.8	16.8	15.9	15.9
Found by Verley's method	24.0	25.5	19.4	20.5	16.9	16.5	14.9	—
Methylol OH calculated	14.3	13.8	6.1	5.8	2.2	1.6	0	0
found	12.2	12.3	6.4	6.2	—	—	—	—
Groups in resin per 1 phenol nucleus	1.7	1.6	0.46	0.42	0.15	0.07	0	0
methylol	0	0	0.83	0.73	1.12	1.15	1.3	1.25
methylene								

* The original solutions of phenol in formaldehyde in Experiments I and II contained 46.5 and 49.8% phenol and 15.4 and 15.8% formaldehyde.

Therefore all the volatile products were completely collected; the loss in weight of the reaction flask with the aqueous phenol alcohols was usually equal to the weight increase of the absorption vessels. Most of the volatile substances were caught in the first receiver. About 1-2% was condensed in the second receiver, while the flask with sulfuric acid absorbed 0.05-0.08% of volatile substances, calculated on the weight of the original phenol alcohols. The dehydration was continued for 3.5-4 hours, and was regarded as complete when anhydrous phenol began to distill and crystallize on the walls of the reaction flask.

The distillate was analyzed for contents of phenol, formaldehyde, and phenol alcohols. It did not give a formaldehyde reaction with sodium sulfite solution but, (like phenol alcohols) it gave a red color with Schiff's reagent; with ferric chloride solution it gave a blue-violet color, which may have been due to a trace of saligenin, which distilled with water vapor in small quantities.

During the dehydration of the phenol alcohols, the water distilled off was accompanied by 1.3-1.7% of phenol, i.e., less than 0.1% of the free phenol present. The quantity of water removed from the phenol alcohols was close to the quantity calculated for the composition of the original mixture.

The table gives the total amounts of free and bound phenol in the dehydrated phenol alcohols, and also of the hydroxyl groups, the total content of which could be calculated by the formula

$$\% \text{ OH} = 0.18a + 0.566b, \quad (1)$$

where \underline{a} is the content of free phenol and of phenol bound in phenol alcohols, and \underline{b} is the content of formaldehyde bound in CH_2OH groups (%).

On the other hand, if only addition of formaldehyde to phenol took place in the formation of phenol alcohols, i.e., if all the oxygen was present in the phenol alcohols in the form of OH groups, then the total OH group content should be 17/16 of the oxygen content.

The data in the table show that the OH group content, calculated on the assumption that all the bound formaldehyde is present in the products in the form of CH_2OH groups, was very close to the value calculated from the oxygen content. This shows that condensation reactions did not occur to any appreciable extent either in the formation of phenol alcohols or in their dehydration, and that all the oxygen was present in the phenol alcohols only in the form of phenolic and alcoholic OH groups. However, the OH group content found by Verley's method was lower than the value calculated from the oxygen content, or by Formula (1). In our opinion, this discrepancy may be partially due to the fact that phenol alcohols are extremely active, and readily undergo condensation even in the cold.

Condensation of phenol alcohols with phenols during storage of undehydrated and dehydrated phenol alcohols was observed earlier by Vansheidt and Vasil'ev [7]. Moreover, partial polycondensation of the phenol alcohols may have occurred during their acetylation on heating under the action of acetic anhydride and acid. To confirm this hypothesis, we synthesized dimethylol-p-cresol and determined the OH group contents both of the compound and of its mixtures with phenol, by Verley's method. In the former case, i.e., in the acetylation of the dihydric alcohol in absence of alkali, it was found to contain about 99% of the theoretical quantity of OH groups. When a mixture of dimethylol-p-cresol with 1.5% NaOH and 25% pure phenol was acetylated, 95% of the OH group content of the mixture was found; this can evidently be attributed to partial condensation of the dimethylol-p-cresol with phenol, with loss of some of the alcoholic hydroxyls.

The content of methylol OH groups in the phenol alcohols was also lower than calculated from the amount of reacted formaldehyde; this can also be attributed to partial polycondensation of the phenol alcohols, since determination of alcoholic OH groups in pure dimethylol-p-cresol by the same method gave results close to the calculated values.

Formation of resoles. For formation of resoles, the dehydrated phenol alcohols were heated at 100° in a Claisen flask, immersed in a water bath and fitted with a capillary tube through which purified nitrogen was slowly passed into the liquid. The flask was connected through a condenser to the absorption system described above, and to a pump which maintained a pressure of 10-2 mm inside the flask. The solution gradually became less mobile on heating, and after about 2.5 hours it became so thick that the nitrogen bubbles ceased to rise to the surface; the reaction was then considered to be complete. The colorless viscous resin in the flask hardened to a solid transparent brittle mass on cooling. It dissolved completely in alcohol, and consisted of a solid resole, which on further heating was converted into an infusible resin.

The table shows that, in the conditions described, the yield of resole from the original anhydrous phenol alcohols was 81-84%; 9-10% of water, and 7-8% of phenol, or about 1/4 of the free phenol present in the phenol alcohols, being distilled off. The resoles contained 6-7% of free and about 70% of bound phenol. The amount of bound phenol was found by difference between the bound and free phenol contained in the anhydrous phenol alcohols, and the free phenol found in the resoles, with a correction for the amount of phenol driven off during the resinification.

The amount of formaldehyde combined in the resole in the form of methylol groups was calculated from its content in the anhydrous phenol alcohols and the amount of water driven off during the resinification, on the assumption that the water was formed only by interaction of methylol hydroxyls with hydrogens of the phenol nuclei, i.e., that the formation of each water molecule is accompanied by the disappearance of one methylol group. It follows from the data in the table that during resinification of the phenol alcohols about 2/3 of the formaldehyde present in the form of methylol groups in the anhydrous phenol alcohols undergoes condensation. The total OH group content of the resoles, calculated by Formula (1), was about 20-20.5%, and coincided with the OH content calculated from the O content. The OH group content found by Verley's method in the resoles was 19-20%, which is close to the value calculated from the oxygen content or by Formula (1).

The small difference (0.6-1.0%) between the calculated and determined contents of the OH groups can probably be attributed to the fact that the resoles were not specially dried, and traces of water liberated during resinification could remain in the resoles and affect the accuracy of the analyses.

To obtain more accurate results, the resins were dried for a long time in a desiccator over sulfuric acid, and then in a vacuum, and then analyzed for the elements and for OH group content by Verley's method. In this case there was exact agreement between the OH group contents found by Verley's method and calculated from the results of elementary analysis.

We also determined the hydroxyl content of one of the resoles by Zerevitinov's (Tserevitinov's) method; the result was close to the OH group content found by Verley's method.

The content of methylol hydroxyls, found by condensation with phenol, was close to the value calculated from the amount of bound formaldehyde, with an allowance for the water liberated during resinification, being about 6% for all three resoles.

The agreement between the OH group content found in the resoles and the amount calculated from the oxygen content of the resin shows that all the oxygen in these resins is present in the form of phenolic and alcoholic hydroxyls, and that therefore the phenol nuclei are linked by methylene bridges and not by dimethylene ether groups in the resoles.

Moreover, if the condensation of phenol alcohols took place by formation of ether groups from methylol hydroxyls, the amount of water liberated during resinification of the phenol alcohols should be half that found.

The results also made it possible to calculate the average number of methylene groups per phenol nucleus in the resoles.

The ratio of the methylene groups to the phenol nuclei was calculated from the formaldehyde content in the dehydrated phenol alcohols and the formaldehyde combined in the form of methylol groups in the resoles, on the assumption that the disappearance of one methylol group during resinification is accompanied by the formation of one methylene bridge. It follows from the data in the table that the molar ratio of CH_2 groups to phenol residues, calculated for resoles I and II, is about 0.8, which corresponds to 5 or 6 phenol nuclei, linked by 4 or 5 methylene groups, in a resole molecule, while the ratio of methylol to phenol groups is 0.45, i.e., the molecule of these resoles contains, on the average, one methylol group per two aromatic nuclei.

Thus, these results confirm the views advanced earlier, according to which resoles are mixtures of methylol derivatives of mesomethylene polyphenols.

Hardening of resoles and chemical nature of resitols and resites. The resoles were heated in powder form for 2.5 hours at 130° in a nitrogen atmosphere under 10-2 mm pressure, the volatile products being collected in the absorption system described above. Under these conditions the resoles were converted into resins of the resitol type, with limited swelling and partial solubility in acetone and alkalis. The distillate did not contain formaldehyde, and consisted of water and phenol.

The table shows that when a resole is heated under these conditions a resitol is obtained in 93-96% yield, up to 1.5% phenol and 4-5% water on the weight of the resole being driven off.

The resitol was a very firm crimson powder, partially soluble in alkalis and organic solvents. The contents of soluble components in the product were determined by extraction of the resin with ethyl alcohol in a Soxhlet apparatus for 18-20 hours; the values ranged from 45 to 13% in Experiments I and II. The resitols contained 83-85% of bound phenol, whereas free phenol (1.41%) was found only in resitol II. The formaldehyde content bound in methylol groups was 2-4%. This was calculated from the amount of formaldehyde bound in the form of methylol groups in the resoles and the amount of water liberated during the hardening, on the assumption that further condensation occurs during hardening at the methylol groups and phenol nuclei. The results so calculated show that about 70% of the methylol groups present in the resoles react during hardening of resoles to the resitol stage.

As in the resinification of phenol alcohols, it is possible to calculate the contents of phenolic and alcoholic hydroxyls from the contents of phenol and of formaldehyde bound in the form of methylol groups in the products formed by hardening of resoles. It was also found that, despite the partial insolubility of these resins, the OH group contents of resitols can be determined by Verley's method. The acetylation of hydroxyl groups in a heterogeneous medium probably proceeds owing to the ability of resitols to swell in organic solvents, including pyridine. The determination was performed as follows: a weighed sample of the resin in the form of a

fine powder (with grains 0.1 mm and less), weighing 0.15-0.20 g, was heated on a boiling water bath for 4-5 hours with 5 ml of an acetylation mixture consisting of 88 parts of pyridine and 12 parts of acetic anhydride. The OH group content found in resitols by this method was about 17%, i.e., close to the value calculated by Formula (1) and from O content.

Agreement between the found and calculated contents of OH groups in resitols shows that the reactions taking place during the hardening of resoles are the same as those which occur in the formation of resoles from phenol alcohols, consisting of interaction between methylol hydroxyls and hydrogen atoms of the phenol nuclei, the only difference being that these reactions not only increase the length of the molecular chains, but result in cross linking. In this case the molar ratio of CH_2 groups to phenol nuclei in the condensation products should be greater than unity. In fact, calculations showed that the ratio is close to 1.15 for resitols I and II.

To obtain resites, the resitols were heated under vacuum in a current of nitrogen for 2.5 hours at 160° .

The table shows that under these conditions resitols liberate 2-3% of water. The products formed were very hard deep-red powders, almost insoluble in alkalis and organic solvents. However, during prolonged extraction (for 48 hours) with ethyl alcohol in a Soxhlet apparatus, resite I lost about 6%, and resite II, 2.6% of its weight. Resite I was still able to swell somewhat in the solvent, whereas resite II did not. The resites contained about 86% bound phenol and apparently did not contain methylol groups, if it is assumed that the water liberated during hardening of resitols is formed by interaction of methylol hydroxyls with phenolic nuclei.

The OH group content of the resites, calculated from the content of bound phenol, was about 15-15.5%, and calculated from the oxygen content, about 15.9-16.0%.

The similar values obtained for the OH group content by these two methods shows that resites contain almost entirely phenolic hydroxyls, otherwise the OH group content calculated by Formula (1), based on the content of bound phenol in the resites, would be lower than that calculated from the oxygen content.

Therefore methylol hydroxyls were present in the resites either in extremely small amounts relative to phenolic hydroxyls, or were entirely absent.

Determination of OH groups in resites by Verley's method only proved possible in the case of resite I, which still retained some swelling capacity; the result was 14.9% OH groups, which is close to the OH group content calculated by Formula (1) and from the O content, whereas the samples which did not swell in pyridine hydroxyl groups could not be detected even after very prolonged heating of the powdered resins with the acetylation mixture.

The agreement between the found and calculated contents of OH groups indicates that during hardening the molecules are cross linked only by binding of methylene groups at the phenol nuclei, and that formation of ether bridges by interaction between phenolic and alcoholic hydroxyls, or from alcoholic hydroxyls alone, did not take place.

The molar ratio of CH_2 groups to phenolic nuclei was 1.30 for resite I, and 1.25 for resite II. Comparison of the average number of CH_2 groups per phenol nucleus in resoles, resitols, and resites shows that this ratio increases in the course of resinification and hardening from 0.8 to 1.3, and that resitols and resites contain more than one CH_2 group per phenol nucleus, as should be the case in the conversion of linear into space polymers.

SUMMARY

1. The chemical processes taking place during the formation and hardening of resole resins were studied by a combined method, consisting of a quantitative study of the consecutive transformations: phenol + $\text{CH}_2\text{O} \rightarrow$ phenol alcohols \rightarrow resole \rightarrow resitol \rightarrow resite, with exact determination of the reacting substances and the products formed, and chemical analysis of the substances at all the conversion stages.

2. A study of the reaction of phenol with formaldehyde in presence of 1% caustic soda at low temperatures confirmed the earlier findings that under these conditions the only reaction is addition of formaldehyde to phenol with formation of phenol alcohols.

3. It was shown that when anhydrous phenol alcohols are heated at 100° in a nitrogen atmosphere they undergo polycondensation with liberation of water from the hydroxyls of the methylol groups and H atoms of the phenol nuclei, with partial binding of free phenol and with formation of resole resins, the oxygen in which is present entirely in the form of phenolic and methylol hydroxyls.

4. When resoles are hardened at 130 and 160°, further polycondensation occurs, with liberation of water from the methylol groups and active H atoms of the resole molecules, with retention of all the phenolic hydroxyls, and with simultaneous formation of space structures, in which phenol nuclei are interconnected by methylene groups in three directions.

5. These results show that, despite the recent views of foreign workers, reactions involving the formation of ether linkages and quinomethide di- and trimers do not occur to any appreciable degree either in the formation or in the hardening of phenol-formaldehyde resoles obtained in the presence of alkaline catalysts.

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SULFONATION OF PHENANTHRAQUINONE TO THE DISULFONIC ACID*

V. I. Sevast'ianov

The sulfonation of phenanthraquinone has been studied little. The known phenanthraquinonesulfonic acids — phenanthraquinone-1-phenanthraquinone-2- [2], and phenanthraquinone-3-sulfonic acid [3], were prepared by oxidation of the corresponding phenanthrasulfonic acids. In an attempt to sulfonate unsubstituted phenanthraquinone by means of concentrated sulfuric acid, the starting material was resinified, with liberation of carbon dioxide and sulfur dioxide [4]. The action of heat on bromophenanthraquinone with 40% oleum at 100° yielded the monosulfonic acid, and with 35% oleum at room temperature, the disulfonic acid of bromophenanthraquinone [5]. The structure of these sulfonic acids was not established.

Titkov was the first to sulfonate unsubstituted phenanthraquinone and to establish the structure of the sulfonic acid formed [6]. He heated a solution of phenanthraquinone in oleum in presence of a small quantity of perhydrol on a boiling water bath and obtained phenanthraquinone-2-sulfonic acid in about 95% yield. Perhydrol was added to prevent the formation of reduction products of phenanthraquinone, which lower the yield and hinder isolation of the sulfonic acid.

The purpose of the present investigation was sulfonation of unsubstituted phenanthraquinone to the disulfonic acid, and determination of its structure.

A solution of phenanthraquinone in 25% oleum was heated in presence of a small quantity of perhydrol on a boiling water bath. The sulfonation product, isolated by the usual method, had a sulfur content corresponding to two sulfonic groups. The yield was 94.5-95%.

The structure of the disulfonic acid was proved by its conversion into 4,4'-dihydroxydiphenyl-2-carboxylic acid and 4,4'-dihydroxydiphenyl. It is known that the action of 10% alkali on phenanthraquinone gives diphenylenglycolic acid [7]. Alkaline fusion converts phenanthraquinone into diphenyl-2-carboxylic acid [8]. Our phenanthraquinonedisulfonic acid gives dihydroxydiphenyl-2-carboxylic acid under these conditions. By its crystal form and melting point (269.5-270°) it corresponds to 4,4'-dihydroxydiphenyl-2-carboxylic acid [9]. Decarboxylation of the latter gave dihydroxydiphenyl, which was identified with 4,4'-dihydroxydiphenyl made from benzidine by the Sandmeyer reaction.

These conversions show that the sulfonic acid obtained was phenanthraquinone-2,7-disulfonic acid. An important property of this compound, like that of the monosulfonic acid described by Titkov, is resistance to oxidation: it is not affected by ten hours of heating with potassium dichromate in 50% sulfuric acid at 60°.

In contrast to anthraquinonesulfonic acids, the sulfonic groups in phenanthraquinone-2,7-disulfonic acid are not replaced by chlorine when it is heated with potassium chlorate in dilute hydrochloric acid.

By analogy with the formation of anthraquinone- α -sulfonic acids by Il'inski's method [10], the sulfonation of phenanthraquinone to the disulfonic acid was tested in presence of mercury. It was found that the latter has no influence on the sulfonation of phenanthraquinone.

EXPERIMENTAL METHODS

Phenanthraquinone-2,7-disulfonic acid. 13 g of phenanthraquinone with m. p. 206-207° was dissolved in 30 ml of 25% oleum and 0.5 ml of perhydrol. The solution was heated with stirring for 1 hour 15 minutes on a boiling water bath. The cooled reaction mass was poured into saturated potassium chloride solution. The precipitate was filtered off and washed with 10% potassium chloride solution and with water.

*Communication I on the sulfonation of phenanthraquinone-9, 10.

The yield was 26.3 g, or 94.7% of the theoretical.

The K salt of phenanthraquinonedisulfonic acid crystallizes from water in the form of long orange needles.

Found %: S 14.47, 14.49. $C_{14}H_6O_6S_2K_2$. Calculated %: S 14.43.

To obtain free phenanthraquinonedisulfonic acid, the reaction mass was cooled, the precipitate was filtered off, pressed thoroughly, and washed with concentrated hydrochloric acid until the wash waters were faintly yellow. The precipitate was pressed, washed with ether, and dried. The product consisted of golden-yellow needles, which did not melt when heated to 350°.

4,4'-Dihydroxydiphenyl-2-carboxylic acid. 25 g of caustic potash was melted with 2 ml of water in a nickel crucible on a sand bath. 5 g of the finely powdered K salt of phenanthraquinonedisulfonic acid was added in small portions, the reaction mass was heated to 315-320°, and held for 15 minutes at that temperature. The cooled melt was dissolved in water and the resinous matter was filtered off. The filtrate was acidified with hydrochloric acid, the precipitate was filtered off, reprecipitated from sodium carbonate solution, and recrystallized from alcohol. The yield was 2.1 g. The crystals were granular, with m. p. 269.5-270°. The melting point of 4,4'-dihydroxydiphenyl-2-carboxylic acid as given in the literature [10] is 270°.

Found %: C 67.74, 67.77; H 4.35, 4.31. $C_{13}H_{10}O_4$. Calculated %: C 67.82; H 4.38.

4,4'-Dihydroxydiphenyl. 2 g of 4,4'-dihydroxydiphenyl-2-carboxylic acid was ground together with 3 g of calcium hydroxide and 5 g of dry river sand. The mixture was heated in an open glass tube at 325-330° until a deposit ceased to form on the inner side of the cold part of the tube. The tube was cooled, the deposit was removed and recrystallized from aqueous alcohol to give needles with m. p. 273.5-274.6°. A mixed sample with 4,4'-dihydroxydiphenyl prepared from benzidine gave no melting-point depression.

SUMMARY

1. Conditions were found for the sulfonation of unsubstituted phenanthraquinone to the disulfonic acid in 95% yield, without admixtures of other isomers.

2. The structure of the disulfonic acid was proved.

I express my thanks to V. A. Titkov for valuable advice.

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*In Russian.

BRIEF COMMUNICATIONS

DISSOLUTION OF ALUMINUM IN CAUSTIC SODA SOLUTIONS.*

A. G. Loshkarev

Our previous paper [1] contained the results of a study of the kinetics of block dissolution of copper, iron, and lead in nitric acid. The present paper contains the results of a study of the kinetics of block dissolution of aluminum in caustic soda solutions.

Aluminum dissolves in aqueous alkalis with evolution of hydrogen and formation of aluminates:

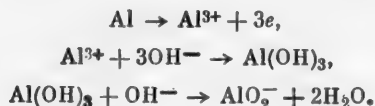


The solution of aluminum in aqueous alkalis has been studied by many workers.

Centnerszwer [2] held that aluminum is dissolved by the action of alkali as the result of a chemical process. Schikorr [3] reached the same conclusion.

The work of Straumanis [4] provided direct evidence for the electrochemical nature of the dissolution of aluminum in alkali solution.

According to Straumanis, the following processes take place at the anode:



The cathode process in the dissolution of aluminum is discharge of hydrogen ions:



Straumanis considers that at low dissolution currents, or local cell currents if such are present, the dissolution rate of aluminum is determined by the anode process of aluminum ionization or by the cathode process of hydrogen-ion discharge.

If the current is considerable, then the chemical reaction of aluminate formation, being the slowest step, determines the dissolution rate of aluminum. In such a case the dissolution rates of different kinds of impure aluminum in alkali solutions should differ little.

The experimental determinations of the dissolution potential carried out by Müller and Löw [5] also provide evidence for the electrochemical nature of the dissolution of aluminum in alkalis. According to their results, the dissolution potential of aluminum depends only on the dissolution rate, the relationship being linear.

The kinetics of the block dissolution of aluminum in caustic soda solutions was studied by the method described in the previous paper [1]. Samples of AV1 grade aluminum were used for the experiments. The alkali concentrations were 6.1, 3.05, and 1.5 g-equiv/liter, and the temperature was 17°. Four drops of the solvent were introduced into the hole in the metal; at 17° the weight of these drops was 0.1916 g of 6.1 N NaOH, 0.1799 g of 3.05 N NaOH, and 0.1716 g of 1.5 N NaOH.

*Communication II in the series on the dissolution of metals and alloys in "block form" (not as shavings).

The weight of aluminum dissolved was determined by means of a photoelectric colorimeter with the use of aluminon.

The results of the experiments are given in Fig. 1.

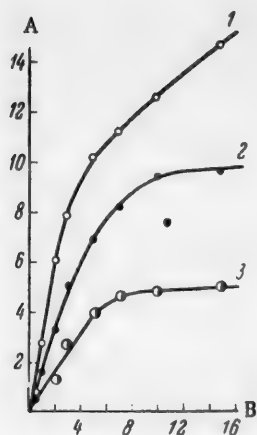


Fig. 1. Kinetics of block dissolution of aluminum in caustic soda solutions at 17°. A) Amount of aluminum dissolved (mg), B) time (minutes). NaOH concentration (N): 1) 6.10, 2) 3.05, 3) 1.50.

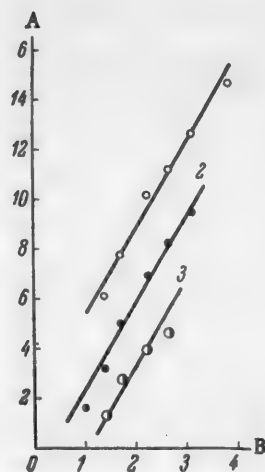


Fig. 2. Nonequilibrium period in the block dissolution of aluminum in caustic soda solutions at 17°. A) Amount of Al dissolved (mg), B \sqrt{t} , where t is the time (minutes) NaOH concentration (N): 1) 6.10, 2) 3.05, 3) 1.50.

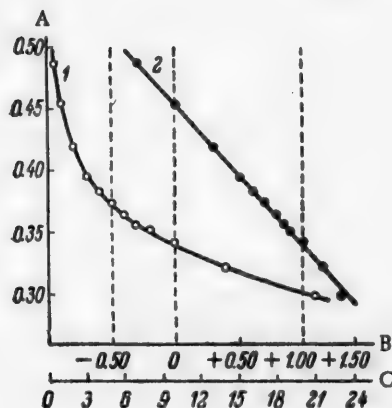


Fig. 3. Variation of the dissolution potential of aluminum in 6.10 N NaOH at 17°. A) negative potential ϕ (in v), B) $\log t$, C) time (minutes). Curves: 1) $\phi - t$, 2) $\phi - \log t$.

For three or four minutes the aluminum dissolves at a constant rate, the amount of metal dissolved being proportional to the time, and after this the solution rate decreases. The explanation for this course of the process is that at the start of the interaction between aluminum and the alkali a layer of aluminum hydroxide is formed on the metal surface; this layer then dissolves, relatively slowly but at a constant rate, as the result of chemical reaction with the alkali passing from the volume of the solution to the metal surface. Therefore the amount of aluminum dissolved is proportional to the dissolution time (linear region of the dissolution curve in Fig. 1). As the alkali concentration in the solution decreases, the rate of diffusion of the alkali diminishes, with a decrease in the dissolution rate of the aluminum hydroxide and therefore of the aluminum.

This second period is characterized by nonequilibrium diffusion of the solvent (curvilinear portion of the curve in Fig. 1). In this case the amount of aluminum dissolved is given by the equation derived in our previous paper [1]:

$$q = \frac{2nF\sqrt{D}}{\sqrt{\pi}}\sqrt{t},$$

where n is the charge of the ion, F is the Faraday number, D is the coefficient of diffusion, t is the time, and $\pi = 3.14$.

* As in original - Publisher's note.

Figure 2 shows, in accordance with the equation for nonequilibrium diffusion, the variation of the amount of aluminum dissolved (q) as a function of the square root of the time (\sqrt{t}). It is seen that the $q - \sqrt{t}$ relationship is linear, so that the above considerations are confirmed by experimental data.

Figure 3 contains the results of experimental determinations of the dissolution potential of aluminum in alkali solutions by the method described previously [1].

The dissolution potential of aluminum increases (becomes more positive), rapidly at first and then more slowly if potassium chloride solution is replaced by alkali solution, and as the reaction proceeds.

The variation of the dissolution potential with time can be represented by the empirical equation

$$\varphi_{Al} = a + b \log t,$$

where $a = -0.567$, $b = 0.112$, φ_{Al} - is the potential (v), and t is the time (minutes).

SUMMARY

It was shown in a study of the kinetics of block dissolution of aluminum in caustic soda solutions it was found that the rate of dissolution of aluminum in alkali is determined by the rate of equilibrium diffusion at the first stage, and by the rate of nonequilibrium diffusion of alkali to the surface of the hydroxide formed on the metal, at the second stage.

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**Original Russian pagination. See C. B. Translation.

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THE THEORY OF EXTRACTIVE RECTIFICATION

V. B. Kogan

Choice of the separating agent is a very important question in relation to extractive rectification. It is generally accepted that to increase the relative volatility of one of the components of a given mixture a necessary condition is that the binary system formed by the separating agent and this component should show greater deviations from ideal behavior than the binary systems formed by the separating agent with the other components. Despite the fact that this principle, which is fundamental in the theory of extractive rectification, is confirmed by numerous practical examples, it has not been rigidly proven and is therefore in the nature of an empirical law. The purpose of this communication is to present a rigid proof of this principle.

It is known [1] that the function Q , proportional to the change of free energy of the solution relative to the pure components as the result of their physicochemical interaction, is represented by the equation

$$Q = \sum_{i=1}^n x_i \log \gamma_i, \quad (1)$$

where x_i and γ_i are the mole fraction and activity coefficient of any component i , and n is the number of components.

Differentiation of Equation (1) gives

$$dQ = \sum_{i=1}^n \log \gamma_i dx_i + \sum_{i=1}^n x_i d \log \gamma_i. \quad (2)$$

By the Duhem-Margules equation,
$$\sum_{i=1}^n x_i d \log \gamma_i = 0. \quad (3)$$

Therefore
$$dQ = \sum_{i=1}^n \log \gamma_i dx_i. \quad (4)$$

Let us consider a system consisting of components 1 and 2 to be separated, and the separating agent (s). As separating agents of low relative volatility are generally used in extractive rectification, it may be assumed that x_s is constant. Then

$$dx_s = 0, \quad dx_2 = -dx_1 \quad (5)$$

and

$$dQ = \log \gamma_1 dx_1 - \log \gamma_2 dx_1 = \log \frac{\gamma_1}{\gamma_2} dx_1. \quad (6)$$

The absolute concentrations of components 1 and 2 may be replaced by their relative concentrations

$$x'_1 = \frac{x_1}{x_1 + x_2} = \frac{x_1}{1 - x_s}, \quad x'_2 = 1 - x'_1 \quad (7)$$

and

$$dx_1 = (1 - x_s) dx'_1. \quad (8)$$

This last expression can be used for writing Equation (6) as

$$dQ = (1 - x_s) \log \frac{\gamma_1}{\gamma_2} dx'_1. \quad (9)$$

The function Q is a property of the system. Therefore its change depends only on the initial and final states, and does not depend on the path taken between these limiting states. Therefore integration of Equation (9) between $x'_1 = 0$ and $x'_1 = 1$, i.e., between the limits of the binary mixture 2-s and the binary mixture 1-s, gives

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2} dx'_1 = \frac{Q_{1s} - Q_{2s}}{1 - x_s}, \quad (10)$$

where Q_{1s} and Q_{2s} are the values of the function Q for the binary mixtures 1-s and 2-s, with concentration x_s of the component s .

As x_s decreases, the compositions of the mixtures 1-s and 2-s, corresponding to the integration limits, approach the pure components 1 and 2, for which $Q = 0$. In the particular case when $x_s = 0$ the system becomes binary, and from Equation (10) we have the equation

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2} dx = 0, \quad (11)$$

derived by Herington [2] and by Redlich and Kister [1]. Since

$$\frac{\gamma_1}{\gamma_2} = \alpha \frac{p_2^0}{p_1^0}, \quad (12)$$

where α is the relative volatility of the 1st and 2nd components, and p_1^0 and p_2^0 are the vapor pressures of these components at the temperature of the system, Equations (10) and (11) may be rewritten as

$$\int_0^1 \log \alpha dx'_1 = \frac{Q_{1s} - Q_{2s}}{1 - x_s} + \log \frac{p_1^0}{p_2^0} \quad (13)$$

and

$$\int_0^1 \log \alpha dx = \log \frac{P_1^0}{P_2^0}, \quad (14)$$

where α_s is the relative volatility of the 1st and 2nd components in presence of the separating agent.

It is readily seen that the left-hand sides of Equations (13) and (14) represent the average volatilities of components 1 and 2 over the entire range of their concentrations, in presence of the separating agent, $(\alpha_s)_{av}$, and in its absence, α_{av} . Therefore Equations (13) and (14) become

$$\log (\alpha)_{av} = \frac{Q_{1s} - Q_{2s}}{1 - x_s} + \log \frac{P_1^0}{P_2^0} \quad (15)$$

and

$$\log \alpha_{av} = \log \frac{P_1^0}{P_2^0}. \quad (16)$$

Subtraction of Equation (16) from Equation (15) gives

$$\log \frac{(\alpha_s)_{av}}{\alpha_{av}} = \frac{Q_{1s} - Q_{2s}}{1 - x_s}. \quad (17)$$

Thus, the average increase of relative volatility due to the presence of the separating agent is determined by its concentration and the values of the functions Q for the binary systems consisting of the components of the mixture and the separating agent. It follows from Equation (17) that the necessary condition for increase of the relative volatility of the first component by the separating agent is that

$$Q_{1s} > Q_{2s}. \quad (18)$$

It readily follows from the definition of the function Q (Equation 1) that with positive deviations from ideal behavior in the binary system 1- s or 2- s ($\gamma_1 > 1$ and $\gamma_s > 1$), Q_{1s} or $Q_{2s} > 0$, and the value of Q_{1s} or Q_{2s} increases with increasing deviation from ideality. For an ideal system ($\gamma_1 = \gamma_s = 1$), $Q = 0$. In a binary system with negative deviations from ideal behavior ($\gamma_1 < 1$ and $\gamma_s < 1$) $Q < 0$, and the value of Q diminishes with increasing nonideality of the system.

It therefore follows from (18) that the necessary condition for increase of the relative volatility of one of the components of a given mixture is that the binary system formed by the separating agent and this component should show greater positive (or smaller negative) deviations from ideal behavior than the binary system formed by the separating agent and the other component. Inequality (18) therefore proves the principle stated at the beginning of this paper. This result may be extended to systems with more than three components.

It must be emphasized that this proof of the relationship between relative volatilities in multicomponent systems and the properties (deviations from ideality) of binary systems is based on the most general thermodynamic considerations. The assumptions used depend only on the limitations on which the Duhem-Margules equation is based. As is known, it is assumed there that the temperature is constant and that the molar volume of the liquid may be neglected relative to the molar volume of the vapor. The second assumption means that the proof is rigid only at not very high pressures, when this assumption is generally accepted. The constant-temperature condition does not make the proof less rigorous. On the contrary, this condition is necessary, as it excludes variations of the vapor-pressure ratio with the temperature and makes it possible to consider changes

of relative volatility caused only by physicochemical interaction of the components, which is the basis of extraction rectification. Equation (17) is important for the theory of extractive rectification, as it can be used for strict thermodynamic determinations of the average increase of the coefficient of relative volatility caused by the presence of a separating agent, from equilibrium data for binary systems.

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THE POSSIBILITY OF ESTIMATION OF THE SPECIFIC SURFACE OF KUKERSITE SHALE FROM ITS HEATS OF INTERACTION WITH LIQUIDS

M. V. Kniga, T. M. Vasil'eva, and K. P. Mishchenko

Institute of Chemistry, Academy of Sciences, Estonian SSR

If the heat effect observed when a solid surface interacts with a liquid, corresponding to the isothermal irreversible enthalpy change of the system (ΔH), was only the heat of wetting as such, it would be possible to determine the specific surface of the wetted object from the magnitude of this effect.

By the second law of thermodynamics, the heat of wetting (ΔH) is equal to the work of adhesion or change of the isobaric potential ΔZ , minus the reversible heat effect of the process, which is equal to the temperature coefficient of ΔZ multiplied by the temperature

$$\Delta H = \Delta Z - T \left(\frac{\partial \Delta Z}{\partial T} \right) \quad (1)$$

Here ΔZ represents the decrease of the surface energy of the solid surface.

Many authors have used values of heat effects, which they assumed to be heats of wetting, for determinations of the specific surfaces of adsorbents [1-3]. When a solid surface is wetted by a liquid, ΔZ is related to the change of surface tension σ . Therefore Equation (1) in relation to such a process may be written:

$$\Delta H = f\sigma - fT \frac{\partial \sigma}{\partial T}, \quad (2)$$

where f is the surface area of 1 g of shale.

If the wetting is incomplete, it is also necessary to take into consideration the cosine of the contact angle ($\cos \theta$). If ΔH is determined by a calorimetric method, if the surface tension of the liquid with respect to air is known, and if $\frac{\partial \sigma}{\partial T}$ is determined, it is possible to calculate f , the specific surface of 1 g of powder, it being first assumed that $\cos \theta = 1$ (the wetting is complete):

$$f = \frac{\Delta H}{\left(\sigma - T \frac{\partial \sigma}{\partial T} \right)},$$

where the denominator represents the enthalpy change of 1 cm² of the surface.

For example, if we know the surface tension of water at $t = 0^\circ$ ($\sigma = 75.64$ dynes/cm) and the temperature coefficient ($\frac{\partial \sigma}{\partial T} = -0.157$) we can calculate, for $T = 273^\circ$, the total surface enthalpy of water

$$\epsilon = \sigma - T \frac{\partial \sigma}{\partial T} = 118.3 \text{ ergs/cm}^2$$

Dividing the measured heat of wetting of dry shale by water [4] ($\Delta H = 0.79 \text{ cal/g}$ or $0.79 \times 4.18 \cdot 10^7 \text{ ergs/g}$) by this value (118.3 ergs/cm^2), we find the specific surface f of the shale:

$$f = \frac{0.79 \cdot 4.18 \cdot 10^7}{118.3} = 1.83 \cdot 10^6 \text{ cm}^2/\text{g}$$

If this method for calculation of the specific surface is correct, and if it is assumed that the interaction of any liquid with shale consists only of wetting, then if water is replaced by another wetting liquid, such as an organic solvent, a similar result should be obtained for the specific surface.

We used this method for calculation of the specific surface from the heat effects in the interaction of shale with methyl alcohol, toluene, ethyl ether, and n-hexane [4, 5]. All the calculations were carried out for "prompachka" shale.

From measurements of the surface tension of methyl alcohol, we can calculate its total surface energy per 1 cm^2 :

$$\epsilon_{\text{CH}_3\text{OH}} = \sigma - T \frac{\partial \sigma}{\partial T} = 48.79 \text{ ergs/cm}^2,$$

when $\sigma = 24.49 \text{ dynes/cm}$; $\frac{\partial \sigma}{\partial T} = -0.094$ [6, 7].

Dividing our value of ΔH , found to be 5.9 cal/g (or $5.9 \cdot 4.18 \cdot 10^7 \text{ ergs/g}$), by 48.79 ergs/cm^2 , we find the specific surface per 1 g of shale:

$$f = \frac{5.9 \cdot 4.18 \cdot 10^7}{48.79} = 4.9 \cdot 10^6 \text{ cm}^2.$$

Knowing the heat effect of interaction of shale with ethyl ether ($\Delta H = 9.0 \text{ cal/g}$) and the surface tension of ethyl ether at 0° , $\sigma = 17.01 \text{ dynes/cm}$ and $\frac{\partial \sigma}{\partial T} = -0.084$ [6, 7], we calculate the specific surface f wetted

by ethyl ether. If $\epsilon_{\text{C}_2\text{H}_5\text{OH}} = \sigma - T \frac{\partial \sigma}{\partial T} = 39.9 \text{ ergs/cm}^2$, then, dividing $\Delta H = 9.0 \text{ cal/g}$, expressed in ergs, by $\epsilon_{\text{C}_2\text{H}_5\text{OH}}$, we have:

$$f = \frac{9.0 \cdot 4.18 \cdot 10^7}{39.9} = 9.38 \cdot 10^6 \text{ cm}^2.$$

Similar calculations were performed for toluene and n-hexane.

For toluene: $\sigma = 30.74 \text{ dynes/cm}$; $\frac{\partial \sigma}{\partial T} = -0.114$ [6, 7]; $T = 273^\circ$; $\Delta H = 6.1 \text{ cal/g}$; $\epsilon = 61.86 \text{ ergs/cm}^2$; and $f = 4.14 \cdot 10^6 \text{ cm}^2$.

For n-hexane: $\sigma = 20.52 \text{ dynes/cm}$; $T = 273^\circ$; $\frac{\partial \sigma}{\partial T} = -0.104$; $\Delta H = 2.37 \text{ cal/g}$; $\epsilon = 48.71 \text{ ergs/cm}^2$; $f = 2.03 \cdot 10^6 \text{ cm}^2$.

The calculated values of the specific surface, and the values determined experimentally by the method of dye adsorption for "prompachka" shale [4] are given in the Table.

* Transliteration of Russian - Publisher's note.

Comparison of Calculated and Experimental Values for Specific Surface

Liquid	Sp. surface calculated from heats of wetting (cm ²)	Sp. surface calculated from dye adsorption (cm ²)
Water	1.83 · 10 ⁵	0.98 · 10 ⁵
Methyl alcohol	4.9 · 10 ⁶	0.98 · 10 ⁵
Ethyl ether	9.38 · 10 ⁶	0.98 · 10 ⁵
Toluene	4.14 · 10 ⁶	0.98 · 10 ⁵
n-Hexane	2.03 · 10 ⁶	0.98 · 10 ⁵

These data show that the specific surface of shale calculated from heats of interaction is relatively close to the value found by direct determination only in the case of water.

The values of f found for organic liquids differ considerably among each other; the specific surfaces calculated from ΔH are about 20-100 times as great as the value determined by the direct method. The greatest deviation is found in the case of ether (a factor of 100). These great deviations cannot, of course, be ascribed to incomplete wetting, as in that case the values of f calculated from ΔH should be smaller and not greater than the true values. In fact, for f to be of the order of $1 \cdot 10^5$ cm² (as given by direct determinations), then in the formula

$$f = \frac{\Delta H}{\sigma - T \frac{\partial \sigma}{\partial T}}$$

the denominator should have a value, in the case of ether for example, of the order of 4000 ergs/cm², since the numerator ΔH is known to within $\pm 0.4\%$ [4]. There can be no question of errors in determinations of σ and $\frac{\partial \sigma}{\partial T}$. With $\sigma = 17$ dynes/cm (in the case of ether), to have $\epsilon = 4000$ ergs/cm² $\frac{\partial \sigma}{\partial T}$ must be about 14.5 or σ must be 3980 dynes/cm. Both of these alternatives are clearly absurd. The differences between the values of f are evidently due to other causes.

It was suggested earlier that the values for the specific surface calculated from calorimetric data (ΔH) can be near to the true values only if ΔH is nothing but the heat of wetting. However, our investigations [4, 5] showed that wetting with ether, methyl alcohol, and toluene is definitely accompanied by swelling and (in the case of toluene) even by dissolution. These processes are evidently accompanied by the corresponding heat effects, which bear no relation to the value of ΔH contained in the thermodynamic Equation (2). Therefore the data in the table fully justify the conclusion, in agreement with our earlier findings [4, 5] that the effect of interaction of liquids with shale measured in our experiments is of a complex nature.

It is significant that in the case of water the values of f found from thermochemical data and by direct determination are in closest agreement, although they differ by a factor of two. With the organic liquids, the difference was least in the case of n-hexane (20-fold). In fact, water is the least likely solvent for the organic substances in shale, and swelling effects likewise cannot have any significant influence.

In the case of n-hexane, which is an organic solvent, although nonpolar, both these effects should be small, but they cannot be completely excluded. It is highly probable that in this case the effects in question can be registered with greater sensitivity by energy determinations than by other methods.

Our results suggest that the conclusions drawn by authors who used Equation (2) without adequate justification for calculations of the specific surfaces of adsorbents must be regarded with caution. There is no doubt that in a number of cases such conclusions may have been rash.

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USE OF RADIOACTIVE ISOTOPES IN INVESTIGATION OF THE KINETICS OF ACCUMULATION OF ELECTROLYTE IONS (SO_4^{2-}) IN ANODIC Al_2O_3 FILMS*

A. F. Bogolavlskii and A. P. Vedernikov

The question of the quantity of electrolyte ions remaining in an anodic Al_2O_3 film is of great applied and theoretical importance. It is important from the applied aspect because electrolyte ions which remain in the protective oxide film may cause its instability and eventual breakdown (crystallization or solidation, in Kislakovskii's terminology [1]). Naturally, breakdown of the protective oxide film must lead to premature corrosion of the protected alloy. It is important theoretically because solution of the problem would provide a basis for clear concepts both of the structure and composition of the protective film, and of the mechanism of its anodic formation.

Despite all this, the problem has remained unsolved and has attracted relatively little attention. This is probably because of the great analytical difficulties involved in experimental solution of the problem. The purpose of the numerous chemical analyses performed on anodic oxide films formed on aluminum alloys [2] was to find the composition of the film from its contents of water and aluminum oxide, and they did not deal with the question of the contents of the ions of the electrolyte used for the anodic oxidation. The question of the influence of various factors (time, temperature, etc.) on the accumulation of ions in the protective film was not considered either. The data available in the literature are fragmentary in character and cannot provide a conclusive answer to the problem. Thus, Bengough and Sutton [3], Sutton and Willstrop [4], Pullen [5], and others report that anodic Al_2O_3 films formed in chromic-acid baths contain traces of chromic acid. In later papers [6] it is stated that such films contain nearly 0.04 g of chromic acid per 1 m^2 of the coated metal. Fischer [7] detected sulfuric acid in a film formed by anodizing by the sulfuric-acid method. According to some reports [3, 4, 5] such films contain variable amounts of sulfuric acid (up to 13.2%). Phillips [2] quotes A. Obricht's 1944 dissertation and states that an anodic Al_2O_3 film formed in an oxalic-acid bath contains up to 3% of oxalic acid, although this is contradicted by earlier data [6]. According to Günther-Schulze [8], protective Al_2O_3 films formed by anodizing in borate solutions do not contain borate ions.

Thus the question of the amount of residual ions in anodic films has not been definitely solved, and is therefore worthy of attention.

In the present investigation an attempt was made to use radioactive isotopes for studying the kinetics of accumulation of residual sulfuric acid in a protective Al_2O_3 film formed in a sulfuric-acid bath. As is known [9], the highly sensitive radioactive isotope method can be used for studying a material without destroying its structure, which cannot be avoided in ordinary chemical analysis. In view of the colloidal nature of anodic oxide protective films, this makes the radioactive isotope method indispensable in studies of the structure and composition of protective films.

EXPERIMENTAL METHODS

The material used was the oxide film formed by anodizing of AD-1M alloy in a sulfuric-acid bath. The specimens were punched out of sheet material, in the form of disks 23 mm in diameter, the sheet thickness being 0.5 mm. The disks were provided with necks for electrical contact ($40 \times 4 \text{ mm}$).

The total anodized surface of each disk was 0.082 dm^2 .

* Communication IV in the series on the anodic formation of Al_2O_3 .

TABLE 1

Results of Determinations of the Absorption of β -Radiation by the Plate Material

Specimen No.	Pulses/minute		Difference from background
	without superposed inactive plate	with superposed plate	
1	118	67	-1
2	742	71	-3
3	474	68	0

Before the anodizing, the specimens were degreased in trisodium phosphate mixture [10] and washed in cold and hot water. The anodic passivation was carried out in 10% sulfuric acid solution containing the S^{35} radioactive isotope (half life 87.1 days [11]). For preparation of "tagged" sulfuric acid, a calculated quantity of 0.7 N solution of active sulfuric acid with specific activity of 3.2 millicuries was added to the solution.

The anodic passivation was carried out in a cell of 200 ml effective capacity. The specimen was placed between two lead anodes. The current density was 2.0 amps/dm². The electrolyte temperature was 37°. The passivation time was varied.

After the anodizing, the specimens were washed for 1 hour with cold water (until no radioactivity could be detected in a sample). The washed specimens were dried with filter paper, and the amounts of radioactive isotope were determined by means of the usual counter unit (V-2) with an end-type counter [9]. The counter plateau was 1450 kv, with 3-4% count efficiency against a uranium standard.

TABLE 2

Kinetics of Accumulation of SO_4^{2-} Ions in Anodic Al_2O_3 Films

Anodizing time (min.)	Weight of film (mg)	Film thickness (μ)	Activity of specimens (pulses/min.)		Total activity (pulses/min.)	H_2SO_4 content (mg)		
			on left	on right		over specimen surface	per unit area (1 dm ²)	on weight of film (%)
1.0	1.5	0.5	30	40	70	0.09	1.04	5.8
3.0	4.0	0.8	159	161	320	0.39	4.70	9.9
5.0	6.3	1.95	214	240	454	0.56	6.75	9.0
10.0	11.7	3.62	365	356	721	0.89	10.70	7.6
20.0	21.4	6.72	581	589	1170	1.45	17.40	6.8
30.0	25.4	7.86	622	589	1211	1.5	18.10	6.2
60.0	27.4	8.52	723	667	1390	1.72	21.20	6.2

Note: 1) To determine the weight of the anodic film, it was dissolved [12] at 93° in a solution consisting of: orthophosphoric acid (sp.gr. 1.561) 45 cc, chromic anhydride 20 g, distilled water to 1 liter, 2) the thickness of the anodic film was found by calculation, 3) the activity of the specimens was unchanged after impregnation with oil, 4) the activity of the comparison standard after neutralization was 86450 pulses/minute.

The amount of sulfuric acid retained by the film was determined from the activity of a comparison standard. This was made from the original 10% solution of sulfuric acid tagged with S^{35} isotope. To prepare the standard, 1 ml of the solution was made neutral to methyl orange with alkali solution, and evaporated to dryness. The subsequent calculation was based on the activity of the dry residue.

As the activity of the anodized oxide film formed in these conditions was determined on both sides of the specimen, it was necessary to determine the absorption of β -radiation by the material of the plate. This was done by superposition of an inactive specimen on an active plate. The results are given in Table 1.

It follows from these results that the β -radiation of the S^{35} isotope is completely absorbed by the specimens of AD-1M alloy. It was therefore permissible to disregard the β -radiation of the layer of active oxide film under the material of the specimen (the lower layer of the film, counting from the end-type counter).

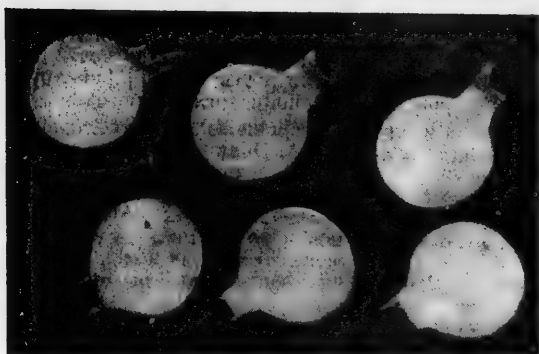


Fig. 1. Autoradiograph of film specimens activated during anodizing.

minute, and then decreases, tending to a certain limit (after about 30 minutes). This suggests that in the most continuous and thin film the electrolyte ions are not present in the adsorbed state [13], but form part of the structure of the oxide material. As the film grows and its breakdown by the bath electrolyte increases, the number of adsorbed ions becomes greater and of structurally bound ions, less. The former are readily washed out of the pores, but the latter are not.

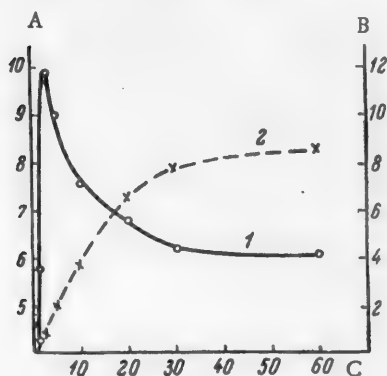


Fig. 2. Variations of the amount of sulfuric acid (1) in the anodic film, and of the film thickness (2) during the anodizing process. A) H_2SO_4 content (%), B) film thickness (μ), C) time (minutes).

2. It is suggested that the anodic film contains, in addition to adsorbed ions, ions which enter the structure of the film substance. These are defined as "structural" ions.

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*In Russian.

**Russian translation.

Data on the accumulation of sulfuric acid in anodic films are given in Table 2 (average results for three specimens).

Figure 1 shows autoradiographs of film specimens activated during the anodizing process. The prints were made by direct contact for 100 hours. Microscopic investigations of the autoradiographs did not reveal any irregularity in the distribution of the radioactive substance in the film.

Variations of film thickness and of the amounts of sulfuric acid in the film during the anodizing are plotted in Fig. 2.

It is seen that increase of the film thickness is not associated with accumulation of residual ions from the electrolyte. On the contrary, whereas the film thickness increases roughly in proportion to the time of passivation, the amount of residual electrolyte per unit weight of film reaches a maximum at the 3rd

It should also be noted that the content of the "structural" electrolyte ions (those forming part of the film structure) increases most rapidly during the first few minutes, i.e., when the densest and thinnest film is formed, which, according to Akimov [14], has no pores of considerable size and which forms the basis for the growth of further layers.

It is probable that thick, loose films contain a certain proportion of electrolyte ions adsorbed in the pores, but also include a certain limiting quantity of ions in the structure of the oxide film, which cannot be removed without destruction of the film.

SUMMARY

1. The kinetics of accumulation of ions in Al_2O_3 formed during anodizing was studied by a radioactive-isotope method; it was found that the accumulation of electrolyte ions in the film is not correlated with increase of the film thickness.

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** Russian translation.

REMOVAL OF PHENOLS FROM TAR WATERS BY MEANS OF VINYL ETHERS

A. V. Bogdanova, M. F. Shostakovskii, and G. I. Plotnikova

Many methods have been proposed for extraction of phenols from tar waters and distillates formed in by-product coke plants. In addition to extraction, methods based on distillation of the phenols in steam with subsequent extraction in alkali [1], on adsorption of phenols by active carbon [1, 2], ash from Winkler gas producers and "Wi" powder have been proposed. For dephenolization of effluents, the methods proposed include ion exchange [3] and polymerization and oxidation of phenols to humus substances by atmospheric oxygen in an alkaline medium. The products formed are allowed to settle; they are then separated from water, burned, and then used as fertilizer [5].

These methods are either not very efficient or involve technical difficulties, and therefore the commonest methods are based on the extraction of phenols in various solvents. The solvents proposed include benzene [6-8], hydrocarbon mixtures, tricresyl phosphate [9], trichloroethylene, light oil [2] and "phenosolvan" * [1]. However, these solvents cannot compete in efficiency with butyl acetate, which is the most commonly used solvent, although it is scarce and expensive. Because of this, and because of the high losses of butyl acetate in the extraction process, other and cheaper solvents are being sought for dephenolization of waste waters.

Recently a method was developed in VNIINP* for extraction of phenols from waste waters and primary-tar distillates, in which the solvents used are intermediate middle-oil fractions of the semicoking and hydrogenation processes. The fact that vinyl aryl and vinyl alkyl ethers and certain of their derivatives are good solvents for phenols suggested that these substances should be studied to determine whether they can be used for extraction of phenols from tar waters.

The availability of vinyl ethers, and the fact that they can be made from phenols and acetylene at the point of utilization, makes the possible use of these compounds for dephenolization of phenolic waters very attractive.

The extraction solvents tested were vinyl butyl ether, vinyl phenyl ether, dibutyl acetal, diphenyl acetal, butyl acetate, and pairs of these substances taken together.

As butyl acetate is widely used in industry at present as an extraction solvent, two-stage extraction by means of this solvent and also with butyl acetate together with one of the vinyl compounds was performed for comparison.

Apart from economic considerations, vinyl ethers and acetals may be recommended as extraction solvents by virtue of their chemical properties. These compounds are difficult to hydrolyze at room temperature, vinyl phenyl ether and diphenyl acetal are hydrolyzed only on prolonged boiling in a strongly acid medium [10]. This is very important, as it means that the loss of solvent during extraction is decreased.

The trials of phenol extraction were performed with tar waters obtained in the semicoking of brown coals from the Ukrainian SSR. The water was filtered through a paper filter and slightly acidified before the extraction. The amount of solvent taken was 25% of the amount of water.

EXPERIMENTAL METHODS

The vinyl ethers and acetals were prepared and purified by the Favorskii-Shostakovskii method in the laboratory of Vinyl Compounds of the N. D. Zelinskii Institute of General Chemistry, Academy of Sciences USSR [11-13] (Table 1).

* All-Union Scientific Research Institute of the Petroleum Industry.

** Transliteration of Russian — Publisher's note.

The following method was used for the extraction of phenols from tar water.

100 ml of filtered tar water, 5 ml of 20% H_2SO_4 , and 15 ml of solvent were taken in a flask with a ground-glass stopper. The mixture was shaken on a mechanical shaker for 30 minutes. It was then transferred to a separating funnel to separate the water. 10 ml of solvent was again added to the water, the mixture was shaken again for 30 minutes and separated. The treated water was analyzed for fatty acids and for volatile and non-volatile phenols by the VNIINP method.

General procedure for determination of phenols in tar water. 10.0 ml of filtered (or extracted) tar water and 30 ml of 20% H_2SO_4 was put into a round-bottomed flask, 0.5 liter in capacity. 500 ml of Distillate A was driven off with steam, with a constant volume of residue (150 ml) in the flask.

TABLE 1

Properties of Materials Used for Extraction

Name of compound	Boiling point (°C)	n_D^{20}	d_4^{20}	Literature source
Vinyl butyl ether	93—94	1.4032	0.7802	[13]
Vinyl phenyl ether	155—156	1.5230	0.9772	[10]
Dibutyl acetal	183—184	1.4085	0.8272	[15]
Diphenyl acetal	146—148	1.5580	1.0808	[14]
Butyl acetal*	(37mm) 121—125	1.3948	—	—

* As in original — Publisher's note.

Determination of volatile fatty acids. Distillate A was heated to boiling for 1 hour in a flask under reflux, and neutralized while hot with 0.1 N NaOH solution against phenolphthalein.

$$\text{The content of volatile fatty acids} = \frac{6 \cdot a \cdot F}{\sim 10},$$

where a is the amount of 0.1 N NaOH used for the neutralization, and F is the correction factor of the NaOH.

Determination of volatile phenols. The neutralized Distillate A was distilled to give a liquid (200 ml with steam and 200 ml without steam) which was diluted by distilled water to 500 ml. For the titration, 50 ml of this solution was taken in an Erlenmeyer flask, followed by 25 ml of bromide-bromate solution (2.7837 g of $KBrO_3$ and 20 g of KBr per liter of water), and 25 ml of 20% H_2SO_4 . The stoppered flask was kept in the dark for one hour. At the end of the bromination 10 ml of 10% KI solution was added, and 10 minutes later the mixture was titrated with 0.1 N thiosulfate solution.

$$\text{Volatile phenols} = \frac{1.567 (a - b) \cdot F \text{ thiosulfate}}{10 \cdot 50} \text{ g/liter}$$

Determination of nonvolatile phenols. The residue in the flask (150 ml) after distillation of the fatty acids and phenols was filtered through a paper filter, which was washed with distilled water; the combined filtrates were made up to 250 ml, and 25 ml of the solution was put into an Erlenmeyer flask, followed by 25 ml of bromide-bromate solution and 25 ml of 20% H_2SO_4 ; the flask was kept in the dark for 3 hours.

At the end of the bromination 10 ml of 10% KI solution was added, the stoppered flask was left for 10 minutes, and the solution was then titrated with 0.1 N thiosulfate solution.

$$\text{Nonvolatile phenols} = \frac{1.567 (a' - b) \cdot F \text{ thiosulfate}}{10 \cdot 25} \text{ g/liter}$$

Data on phenol extraction are given in Table 2.

TABLE 2

Results of Experiments on Phenol Extraction

Solvents used	Present after extraction (g/liter)			Amount extracted (%)		
	volatile fatty acids	volatile phenols	nonvola- tile phenols	volatile fatty acids	volatile phenols	nonvola- tile phenols
Original water, without extraction	6.65	1.73	3.15	—	—	—
Vinyl phenyl ether	} 4.55	0.48	1.64	38.0	72.3	48.0
Dibutyl acetal						
Diphenyl acetal	} 4.47	0.62	1.56	32.8	64.2	50.5
Vinyl butyl ether*						
Butyl acetate*	} 5.35	0.32	1.59	19.6	81.6	49.6
Butyl acetate*						
Vinyl phenyl ether	} 4.9	0.23	1.48	26.4	86.8	53.1
Butyl acetate*						
Diphenyl acetal	} 6.5	0.31	1.57	18.3	82.2	50.2
Butyl acetate*						
Vinyl phenyl ether	} 4.11	1.41	2.36	38.2	19.0	25.1
Vinyl butyl ether*						
Dibutyl acetal	} 4.3	0.78	1.89	36.0	55.0	40.0
Vinyl phenyl ether						
Vinyl butyl ether*	} 5.4	1.41	2.20	19.0	19.0	31.0
Butyl acetate*						
Butyl acetate*	} 4.02	2.3	1.56	39.1	—	50.5
Vinyl butyl ether*						

* As in original — Publisher's note.

SUMMARY

Laboratory tests were carried out on vinyl phenyl and vinyl butyl ether, and their acetals, to determine their stability as solvents for dephenolization of tar waters obtained in the semicoking of brown coals of the Ukrainian SSR; it was found that these compounds can be used independently or together with butyl acetate.

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THE AUTOOXIDATION OF KEROSENES FROM THE CRACKING PROCESS

Ia. B. Chertkov and V. N. Zrelov

Scientific Research Institute of Fuels and Lubricants

It was shown in our earlier papers that when hydrocarbon fuel fractions in the ligroine and kerosene range are stored for a long time, they undergo low-temperature oxidation, with formation of oxygen compounds containing various functional groups. A considerable proportion of the oxidation products was found to consist of unsaturated aromatic alcohols.

The least stable hydrocarbons were oxidized; these primarily include compounds, the structure of which comprises aromatic rings with unsaturated side chains.

Mixed with the oxygen compounds, compounds containing sulfur and nitrogen were also present; the carbon skeleton of these compounds was similar to that of alcohols [1-4].

It is known that some oxygen compounds are present in oils and pass into fuels during processing, before oxidation products formed from the fuel hydrocarbons during storage begin to accumulate.

Not enough is known about the influence of the oxygen compounds entering the fuel during its production, on its subsequent oxidation during storage, and about the manner in which the oxidation processes develop in the fuel.

In this investigation an attempt was made to evaluate separately the nature of the oxygen compounds present in the fuel as produced, and accumulating during prolonged storage, and to determine their influence on the autooxidation of fuels.

Cracked fractions from Volga and Baku oils, the characteristics of which are given in Table 1, were used for the investigations.

TABLE 1

Characteristics of Cracked Fractions

Characteristics	From Volga oils		From Baku oils
	Bashkir ASSR	Tatar ASSR	
Density d_4^{20}	0.827	0.816	0.8539
Boiling range ($^{\circ}\text{C}$)	130—279	104—245	105—304
Molecular weight	165	150	173
Iodine number (in g I_2 /100 g).	46	44	53
"Factual" tars (in mg/100 ml)	18	12	124
Acid number (mg KOH/100 ml)	0	0	7
Light absorption (%)	3	1.5	100
Refractive index (n_D^{20})	1.4620	1.4590	1.4775
Sulfonable matter (%)	40	40	50
Sulfur content (%)	0.94	0.78	0.21

Two batches of the cracked fractions were stored under the usual conditions; under an awning in the open air, in three-liter dark bottles, in contact with strips of No. 3 steel with area equivalent to the relative area of contact when the fuel is stored on 200-liter barrels made from the same material. Air access was through a glass capillary.

One batch consisted of the original fuel, and the other was treated chromatographically with silica gel to remove the tarry matter.

The tarry matter was separated from the fuel on ShSM silica gel, 28-65 mesh, at volume feed rate 0.5 hour^{-1} . Isopentane was used for desorption of the hydrocarbon fraction, and methanol for desorption of the nonhydrocarbon material.

After 18 months of storage, the nonhydrocarbon portion, consisting mainly of oxidation products of the hydrocarbons, was isolated from both batches, and studied (Table 2).

TABLE 2

Characteristics of the Nonhydrocarbon Portion of Cracked Kerosenes

Characteristics	From Volga oils				From Baku oils	
	Bashkir ASSR		Tatar ASSR			
	original	percolated through silica gel	original	percolated through silica gel	original	percolated through silica gel
Yield of nonhydrocarbon compounds (mg/100 ml)	670	2520	533	2400	1805	8080
Density (d_4^{20})	1.037	1.030	0.9727	1.0345	1.0490	1.0444
Molecular weight	261	218	183	266	238	251
Iodine number (I_2 /100 g)	75	54	146	54	130	50
Refractive index (n_D^{20})	1.5372	1.5220	1.5281	1.5385	1.5300	1.5330
Hydroxyl number (mg KOH/g)	100	126	172	83	127	87
Acid number (mg KOH/g)	12	14	2	17	8	11
Ester number (mg KOH/g)	23	49	10	66	34	51
Carbonyl number (mg O_2 /g)	7	24	0	13	0	10
Sulfur content (%)	4.9	2.8	6.7	2.4	1.25	0.3
Boiling range at 5 mm Hg ($^{\circ}\text{C}$)	60-150	45-125	66-140	56-110	70-150	60-125
Distillate yield (%)	70	65	73	70	78	75

It is seen that fresh oxygen compounds accumulated at a high rate in the fuel from which the nonhydrocarbon fraction, including oxygen compounds, had been previously removed. The amount of freshly formed oxygen compounds was 4 times the amount extracted from fuel not subjected to preliminary purification and then stored for the same period.

The oxygen compounds were generally similar.

It is quite obvious that such very high rates of formation of oxygen compounds are due not only to the presence of unstable hydrocarbons which are susceptible to oxidation during storage, but also to the absence in the fuel, at the start of the storage period, of oxygen compounds which inhibit the oxidation process. The nonhydrocarbon portion formed in fuels previously percolated through silica gel had lower iodine numbers. It seems likely that oxidation processes were very much more rapid in fuels deprived of the protective action of certain oxygen compounds. A much wider range of hydrocarbons was oxidized than was the case in the original cracked fractions.

Under these conditions processes leading to formation of acids, and hence compounds with ester groups, were also more rapid.

The decrease in the contents of sulfur compounds in the tarry fraction of fuels stored after preliminary purification is noteworthy.

The boiling ranges and yields of distillable oxygen compounds differed little.

SUMMARY

1. The nonhydrocarbon portion present in kerosene cracked fractions, which consists to a considerable extent of neutral oxygen compounds, has a certain inhibiting effect on autocatalytic oxidation of hydrocarbons.
2. Removal of this nonhydrocarbon portion results in a sharp increase of the oxidation rate, with oxidation of a wider range of hydrocarbons.
3. Oxygen compounds, of similar characteristics in different types of kerosene cracked fractions, may accumulate at considerable rates in the nonhydrocarbon fractions; they can be regarded as a possible source of new chemical compounds, worthy of further investigations and determinations of their practical utility.

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SYNTHESIS OF 6-METHOXYQUINOLINE

B. I. Ardashev and V. I. Minkin

6-methoxyquinoline is the starting material in the synthesis of a number of antimalarial drugs and valuable cyanine dyes. Its preparation is based on the Skraup reaction [1], which proceeds much more vigorously in this case than in the synthesis of quinoline and methylquinolines [2]. A common disadvantage of all the early methods for the synthesis of 6-methoxyquinoline [2-4] is the difficulty of controlling the reaction reliably, and the consequent risk of explosion; the usual methods for moderating the reaction rate (additions of FeSO_4 , CH_3COOH etc.) are not effective. Evolution of heat cannot be avoided if large quantities are used; if the reaction is carried out by Cohn's method [5], a long time (40-50 hours) is required and considerable resinification occurs [6]. Direct additions of acrolein [7] are inconvenient in production, and the yields obtained are low (13%). Attempts to control the reaction by gradual addition of sulfuric acid to a mixture of the other components [8] are not very effective if large amounts of starting materials are used, because of the presence of excess unreacted amine, which can react exothermically with the acrolein formed from glycerol.

These difficulties can be avoided by gradual addition of a mixture of amine, sulfuric acid, and glycerol to the oxidizing agent, in accordance with Walter's modified method [9]. However, because of the unsatisfactory yield, the conditions must be different from those used in the preparation of quinoline by this method, otherwise the yield does not exceed 20-25%.

The product is isolated either with steam superheated to 110-120°, when p-anisidine does not distill to any appreciable extent, or directly from the reaction mixture with subsequent purification by means of phthalic anhydride [10].

The formation of 6-hydroxyquinoline by demethylation of 6-methoxyquinoline, which may form 1/3 of the reaction product under harsh synthesis conditions [11], and of 6-methoxy-8-hydroxyquinoline, which is sometimes formed in this synthesis [12], was not observed in our experiments.

EXPERIMENTAL METHODS

22 g of p-nitroanisole, which was heated to 170°, was put into a two-necked flask fitted with a thermometer and a reflux condenser (and also with a stirrer in experiments with large quantities). A mixture of 26 g of p-anisidine, 25 ml of 90% H_2SO_4 , and 120 g of glycerol, maintained at the temperature of a boiling water bath, was then gradually added through the condenser. After the first portion was added, the mixture separated into two layers; when these became mixed, the mixture boiled. At the end of the addition the temperature of the boiling mass was 145-152°. The boiling was continued for 4.5-5 hours more, when the temperature fell to 133-136°. The mixture was cooled to 70-80°, diluted with 250 ml of water (In other experiments p-nitroanisole was distilled in steam, the mixture was made alkaline by the addition of 50% NaOH solution, and 6-methoxyquinoline was distilled with superheated steam), and p-nitroanisole was extracted in benzene. The acid solution was made alkaline by addition of 20% NaOH, and extracted twice with large portions (to ensure better separation) of benzene, which were then filtered to remove resinous matter. After distillation of the benzene, the residue was dissolved in 300 ml of ether and treated twice with phthalic anhydride, in portions of 25 g and 15 g, until the latter was dissolved. The ether solution was washed with 10-15% NaOH solution, when admixtures of primary amines were removed in the form of phthalamic acid salts, then with water, and dried with potash.

The ether was driven off and the residue was distilled. The yield of 6-methoxyquinoline was 21.5 g (64%), b. p. 127-130° (5 mm), and 279-284° under atmospheric pressure.

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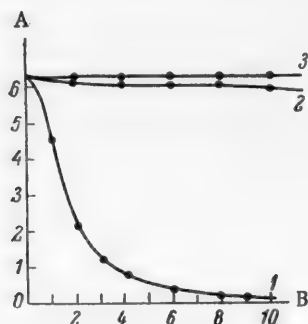
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INFLUENCE OF OXYGEN ON THE DEGRADATION OF POLYMETHYL METHACRYLATE

O. P. Koz'mina and A. N. Shirshova

Lebedev [1] showed that vinyl polymerization is a reversible process. The depolymerization of methyl methacrylate polymer is used in practice for regeneration of the monomer, which is obtained in high yields by pyrolysis of waste plastics. In addition to methyl methacrylate, the pyrolysis products were found to contain

methyl alcohol, carbon dioxide, and other decomposition products [2]. Votinov, Kobeko, and Marei [3] showed that the rate of thermal decomposition of linear polymers has a high temperature coefficient, and found that the rate is higher in presence of air. The view has been advanced that depolymerization proceeds stepwise. Simha [4], Brockhaus [5], believe that the reaction proceeds by a chain mechanism. Jellinek [6] assumes that weak, easily broken bonds exist in the chains. According to Grassie [7], the process occurs at the ends of the polymer molecules, and takes place mainly at 220°.



Thermooxidative decomposition of polymethyl methacrylate. A) Molecular weight $\cdot 10^6$ (calculated from the intrinsic viscosity), B) heating time (hours). Heating at 200°; 1) In oxygen, 2) ditto, with addition to 1% of phenyl- β -naphthylamine, 3) in nitrogen.

In heating polymethyl methacrylate at 200°, we found that degradation occurs only in presence of oxygen; if purified reprecipitated samples were used, the degree of polymerization fell sharply without separation of the monomer.

This last fact shows that the bonds are broken not at the ends but within the polymer molecule, probably at the points where peroxide groups are formed by the action of oxygen.

Polymethyl methacrylate does not undergo degradation when heated in nitrogen under the same conditions. Additions of antioxidants — secondary aromatic amines and phenols (diphenylamine, phenyl- β -naphthylamine, resorcinol salicylate, etc.) — make it stable to heat even in oxygen. The inhibiting effect depends on the nature of the inhibitor, the amount added, its volatility, etc.

Samples of polymethyl methacrylate of different molecular weight were investigated. The polymers were reprecipitated from solution in acetone or chloroform, thoroughly washed with ligroine free from olefins and aromatics, and dried to constant weight in a current of nitrogen under low pressure. The samples were heated in a vessel containing a porous plate through which air, oxygen, or nitrogen was passed from below. As the oxidation proceeded, the intrinsic viscosities of the polymer solutions were determined, and the amounts of volatile reaction products and absorbed oxygen were found in parallel experiments. The decomposition rate increased with increasing molecular weight of the polymer; for example, samples of molecular weight $6 \cdot 10^6$ and $2 \cdot 10^2$ reached the same degree of degradation after 4-5 hours. The rate of thermooxidative degradation of a commercial sample is plotted in the Figure. It might be thought that degradation occurs owing to incomplete removal of volatile matter (monomer) and peroxide compounds or groups from the polymers. However, the same results were obtained with samples previously heated for a long time in nitrogen, and after dialysis of the samples.

Despite the considerable decrease of viscosity, the polymers did not melt on heating, retained the appearance of the original powders, and only traces of condensate with an odor of the monomer were found in the traps. No volatile products were liberated when the polymers were heated in nitrogen.

To measure the oxygen absorption, samples were heated in a closed system containing an oxygen buret, with internal circulation of the gas phase through absorbers to remove gaseous reaction products.

Under these conditions the samples absorbed about 2 ml of oxygen per gram of substance in 5 hours at 200°, with oxygen circulated at 3 liters/hour, while the intrinsic viscosity fell to 0.5. The elementary composition of the samples changed little in the process; for example, for sample No. 2:

Found before heating	%: C 59.82; H 8.13.
Found after 10 hours of heating	%: C 59.42; H 8.36.
$C_6H_8O_2$. Calculated	%: C 59.96; H 8.06.

All these results apply to dry purified polymer samples. Totally different results are obtained if the same samples are heated in presence of residual monomer, solvent, and moisture. In that case the substance liquefies within 3-4 hours from the start of heating, the monomer is liberated, and the gases contain formaldehyde, and carbon monoxide and dioxide. The same is found if the polymer is heated in block form.

SUMMARY

1. The degradation of polymethyl methacrylate on heating (at 200°) is the result of its reaction with oxygen, and can be prevented by addition of antioxidants. In absence of oxygen, the degree of polymerization of methyl methacrylate does not decrease after many hours of heating at 200°.
2. The substances present in technical polymethyl methacrylate (monomer, plasticizer, etc.) greatly accelerate its depolymerization in oxygen.

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BOOK REVIEW

GRANULATED BLAST-FURNACE SLAGS AND SLAG CEMENTS

P. P. Budnikov and I. I. Anachkov and I. I. Znachko-Iavorskii

Industrial Construction Press, Moscow (1953) p. 224

The book by P. P. Budnikov and I. I. Znachko-Iavorskii was recently discussed in the Department of Silicate Technology of the Prague Institute of Chemical Technology. The reason for this is the increased interest in better utilization of blast-furnace slags, which has been recently displayed in our country.

Members of the Cements Section of the Department of Silicates carried out a comparative study of the world literature on the subject, and considered the above-named book to be the best. Russian books are very popular in our country; they are read freely and therefore do not require translation.

Czechoslovak readers would be extremely glad to see a new edition of this valuable work; the most desirable additions must be noted here. The most important relates to the influence of the equipment and granulation method on the properties of the slag. Details of the practical operation of the granulators, and of practical applications of blast-furnace slags are also of great interest to us.

It would also be very useful to add new data on crystal chemistry and the latest advances in cement science, particularly in the field of the kinetics of setting and hardening of different types of cements in relation to the type of slag and the process by which it is made; on rheological properties, and on the aging of concretes made from these cements.

We in Czechoslovakia hope that a second edition of this book, which is detailed, rich in factual data, and on the whole very good, will appear in the near future.*

Prague

Rudolf Barta

* Written for publication in the Soviet technical press.

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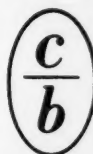
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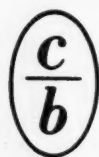
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